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關鍵字 奈米鑽石、重金屬離子、吸附

作者簡介



夏志豪,今年為建中高二學生,16 歲,從小學到目前高中階段皆從事科學研究,故可謂:科展占滿童年的實例。回首往年,國小第一次從事不同「溶液」(果汁… 等)的導電度顯示方式,當時,即是 LED 商品的首次接觸。國中,即開始對重金屬 汙染偵測與土壤整治實驗利用 LED 與積體電路作分析,高中並慢慢地轉向純粹對 於源頭水溶液進行偵測的分析,高一時,利用水溶液的電阻變化作定性與定量分 析。而,現在的我,一位高二學生,不斷尋找大學端與中研院資源,增廣見聞, 感謝教授及台大與中研院的協助,使我如願得到關於處理重金屬汙染的新材料分 析結果。

如第一段所述,得知化學領域除了物化(理論)尚無深入探討外,其他皆有機會 接觸。如今,我已下定決心念化學,更希望能於大學之前將物化軌域與其方程式 稍有了解,讓自己對於化學領域選擇有更明確的答案。萬分感謝!

奈米鑽石性能對於重金屬吸附之應用

摘 要

奈米鑽石之多官能基、介面電位負值(PH=7時)…等性質使本組考慮其吸附重 金屬離子之可行性。本研究目的在於利用奈米鑽石吸附重金屬離子及探討重複利 用性。

將硝酸鉛、鋅、鎳、銅、鈷與鐵離子及錯離子水溶液配製奈米鑽石混合懸浮 液。本實驗利用共扼焦顯微鏡了解奈米鑽石之生物共生與吸附特性。於重金屬吸 附上運用LM324系統、及ICP-MS測量溶液濃度, 且用SEM觀察表面。

研究結果顯示, 奈米鑽石具優越吸附離子能力, 吸附前後奈米鑽石表面在巨 觀與表面微觀上有顯著改變; 且再利用性極佳, 可利用硝酸置換出金屬離子。故 奈米鑽石應可作為具再利用性之吸附材料。

Application of Nanodiamonds Characteristic

on Heavy Metal Adsorption

Abstract

Nanodiamond (ND) has superior adsorption characteristics, biocompatibility, abundant functional group and countless terminal points originating from the diamonds' sp³ orbitals, making our research term considering the possibility of heavy metal adsorption.

The main experiment was focus on the nanodiamonds' adsorption characters. On bio aspect, we used confocal microscope to observe the changing on the algae. We also assumed that nanodiamond has the ability to adsorb heavy metal ions. With the dispersion of nanodiamond in solutions containing Lead (Pb^{2+}), Zinc (Zn^{2+}), Cobalt (Co^{2+}), Iron (Fe^{3+}), Copper (Cu^{2+}), Nickel (Ni^{2+}) and some complexes aqueous solution, we discovered instantaneous sedimentations of compounds from nanodiamond and metal ions. We used LM324 system to measure the conductivity of our samples to reflect its' contents after the addition of solutions containing metal ions. We also used SEM to scan the surface of nanodiamond precipitates before and after reactions.

Our results show that nanodiamond has superior adsorption capability of metal ions. The SEM pictures show significant changes on the surface of nanodiamond after compounding with metal ions. With the addition of nitric acid, the metal ions will be dissolved. This makes it possible that nanodiamond can be re-used as an effective metal removal agent.

一、 前言

(一)研究動機

新聞報導常出現重金屬汙染課題。各地工廠不定時排放重金屬離子廢液 致使農田汙染,其嚴重性亦成為世界憂患。近來,緣色化學的概念盛行, 尤在美洲地區極為重視,透過課程對其十二個原則了解,深刻體會幾點: 無毒、抓害、監控、環境回復…等的環境保育觀念。

近年螢光奈米鑽石(以下簡稱FND)注入動物細胞追蹤研究如火如荼展 開。本組在先前從事FND與黃花狸藻的追蹤研究中,觀察到狸藻外部之吸 附情形【圖1】,推想FND可能有吸附重金屬離子之用。於先前科展,本 組即研究簡易重金屬汙染監測法,利用水溶液內電導度的變化,做為重金 屬離子濃度指標、快速分辨重金屬離子種類。本次實驗結合上述的研究結 果,進一步運用奈米鑽石材料於重金屬環境整治上之研究。





(二)研究目的

- 1. 以共扼焦顯微鏡的顯像探討黃花狸藻(Utricularia aurea)吸附 FND 的功能。
- 2. 研究 ND 吸附重金屬離子的效率。
- 3. 研究吸附重金屬後 ND 表面的結構。
- 4. 研究重複使用 ND 以吸附重金屬離子的可行性。



(一)研究設備與藥品1.研究設備



2. 研究藥品



(二)研究方法與系統概述

- 1. 文獻探討
 - (1) The properties and applications of nanodiamonds【註6】 於本篇文獻中清楚了解奈米鑽石製造過程、特性及其應用方 面之推展。係因此篇文章(p.16)圖片提及奈米鑽石官能基的特性, 鑑於許多有機官能基離子具孤電子對且該分子的介面電位為負 之特質,發想關於錯離子產生的問題與討論。亦因其中提及生 物共生性介紹,故本實驗提出生物共生性研究與討論。
 - (2) 居禮夫人的寶石:螢光奈米鑽石【註4】

此篇對螢光奈米鑽石有詳盡解說與特徵提供,對初始實驗黃 花狸藻藻體奈米鑽石追蹤具開導作用。

(3) 水生開花食蟲植物絲葉狸藻捕蟲囊構造及共質體運輸

【註 2】 在理解此篇時,得到黃花狸藻的相關實驗記錄與 觀察重點,是為本次實驗之開導。

- (4)利用 IMS 即時顯示系統建立資料庫,在重金屬汙染監測上之應用【註3】 本組透過此篇方式進行更正與改良(詳請見討論一)用以測試步驟二之導電率檢測法。
- (5) 奈米粒子對細胞與生物之毒性及其分布【註5】 由其中議題及奈米鑽石,本組隊其結果產生毒性探討,並 做相關查詢與實驗。
- (6)應用吸水高分子螯合重金屬離子及奈米銀的製備【註1】 對其無法吸收重金屬錯合物之問題並觀察本組研究成果。

2. 研究方向概述

(1) 文字敘述

先以 FND 來進行追蹤黃花狸藻,透過共扼焦顯微鏡及肉眼觀察 並討論未來方向,提出兩點:一、透過奈米鑽石特性及觀察結果直接進 行不同濃度硝酸鉛水溶液及植物知吸附與保護作用。二、直接將等量奈 米鑽石放入,並從事奈米鑽石與重金屬的吸附與濃度關係。後經第一階 段實驗數據得知奈米鑽石的加入確實對整體溶液造成影響,但當時尚未 有規律性的結果。故第二階段,本組操作離心機以觀察去除奈米鑽石對 本組之影響後前後數據差異。其後即以酸洗後的奈米鑽石來做相關實驗, 並指出關於不同重金屬離子差異與分別及討論錯離子化合物的吸附關 係。透過成果再討論於科學與工程利用上的重要指標並追溯回錄色化學 議題。



(三)研究步驟

- 1. 植物取得、養殖及 ND 與 FND 溶液配製
 - (1) 植物取得
 - A. 透過【註3】文獻之詳盡介紹,對黃花狸藻捕蟲囊之結構與 方向興趣增長。
 - B. 在花市與賣水生植物的阿姨購買兩株黃花狸藻。
 - (2) 一般養殖(實驗前)【圖 15】A. 以自來水養殖即可。



- (3) ND與FND溶液配製【圖16】
 - A. 以電子秤秤重。
 - B. 加水並放入超音波震盪器5分鐘以將奈米鑽石聚集打散。

【圖 16】 配製



- 2. 導電率測試【圖17】
 - 將一個長、寬、高為4、1.5、2.5 公分之壓克力箱加入帶測 溶液。
 - (2) 以 LM324 積體電路對其電壓與電流測量,並透過 Excel 計算 電阻與電導率,並繪表討論結果。
- 螢光奈米鑽石對植物之顯像分析
 (1) 紅色螢光



📶 【圖 18】溶液與植株生長環境

A. 將步驟一所配製之紅色奈米螢光鑽石溶液取出並稀 釋為以下濃度: 125 µg/ml, 100 µg/ml, 75 µg/ml, 50 µg/ml, 25 µg/ml, 5 µg/ml。【圖 18】

- B. 取出植株並放入溶液中。【圖 19】
- C. 取 125 µg/ml, 5 µg/ml 中的捕蟲囊於共扼焦顯微鏡下 做顯像分析,其餘預備做實驗四之實驗。



- (2) 綠色螢光
 - A. 將步驟一所配製之綠色奈米螢光鑽石溶液取出並稀釋 為以下濃度: 125 µg/ml, 100 µg/ml, 75 µg/ml, 50 µg/ml,
 - 25 µg/ml。【圖 20】
 - B.取出植株並放入溶液中。
 - C.取所有植株之捕蟲囊於共扼焦顯微鏡下做顯像分析,並 將剩餘植株做實驗四之研究。。



- (3) 紅、綠色混合螢光
 - A. 將綠色奈米鑽石溶液加入紅色奈米鑽石配製成紅、綠
 色混合螢光溶液。
 - B.加入植株,放置一月,並觀察其奈米鑽石顯色情形。
- 4. 植株、奈米鑽石作用與吸附重金屬之量質分析、討論
 - (1) 導電率差異
 - A.將實驗三之綠色螢光奈米鑽石植株溶液倒出,並加入 100ppm 硝酸鉛水溶液。【圖 21】
 - B.靜置1天,分別以實驗二之導電率檢測方式測量導電曲線。



- C. 做完 A 實驗後,將藻體放入水中。
- D. 將植株至於共扼焦顯微鏡下,對其做細部差異比較。
- 5. ND 吸附重金屬研究一(未酸洗之奈米鑽石)
 - (1) 第一階段
 - 將定量奈米鑽石分為四管。【圖 22】 A.
 - B. 以水調製飽和溶液後,稀釋硝酸鉛水溶液,分別調 配出硝酸鉛濃度 0ppm, 50ppm, 100ppm, 200ppm 之奈 米鑽石硝酸鉛水溶液。【圖23】
 - C. 放置一天及五天,並運用步驟二之電導度檢驗法測 其導電曲線。



- (2) 第二階段(離心後)
 - A. 將第一階段之試管以離心機10000轉/分運作約20分鐘。 【圖 24】
 - B. 對離心尚未完全(註 1)之試管再增加離心時間 30 分 鐘。
 - C. 取出上層清澈水溶液,進行步驟二之導電率測試運作 10 分鐘後,再以 Excel 繪表。
- 註 1:尚未完全即是指該溶液在燈照下仍有光束。

註 2:對試管(無 Pb)由於離心 2 次後仍呈混濁溶液,暫不做下步實 驗。



- 6. ND 吸附重金屬研究二(酸洗後之奈米鑽石 ND-COOH)
 - (1) 導電率測試
 - A. 將步驟一配製之奈米鑽石溶液與硝酸鉛、硝酸鎳及硝酸锌水溶液混合稀釋為奈米鑽石濃度 500~1000 μg/ml 及重金屬離子溶液 50ppm, 100ppm, 200ppm 之 混合液體。
 - B. 配製各種金屬離子及其對應濃度之水溶液,不加奈米 鑽石視為對照組。
 - C. 放置一天半後,取出上層尚為澄清之溶液,並以步驟 二之導電率檢測方式測量導電曲線。
 - (2) 微觀觀察
 - A. 透過本組所發現的沉澱現象取出沉澱物。
 - B. 將樣本取出滴於一玻片上,並加熱烘乾。
 - C. 在圓形平面上塗抹黏膠並將預設之乾樣本黏起,備 用,或以刮勺刮下樣本粉末。
 - D. 將物品置於電子顯微鏡觀察其細部大小、差異與結構。
- 7. ND 吸附濃度差比較測量(多種)
 - (1) 一般硝酸金屬溶液配置
 - A. 將 Pb(NO₃)²、Ni(NO₃)²、Cu(NO₃)²、Co(NO₃)²與 Fe(NO₃)³
 配置成 4000ppm(註 1)備用。
 - B. 將奈米鑽石水溶液(2mg/ml)加入上述 4000ppm 水溶液 註 1:4000ppm 為本組配置值,由於實驗會有些許誤差,本組亦 將原始溶液 ICP 測量,該值則為準確值。
 - (2) 配置重金屬錯合物
 - A. 在硝酸鈷加入過量的氨水配置至完全無沉澱為止。
 - B. 加奈米鑽石以從事吸附效率研究



- (3) ICP-MS 測量
 - A. 將樣本離心後備用。
 - B. 配置標準溶液 (介於 10, 20, 30, 40, 50ppb)。 【圖 26】



- C. 取出樣本分別將其稀釋至 30ppb 左右(註 1) 【圖 27】。
- D. 跑 ICP-MS。



【圖 27】樣本稀釋



F. 對實驗數據做分析。

註 1:ppb 等級配置原因為 ICP-MS 感應度高,須以較小的濃度防止機器損壞。

三、研究結果與討論

(一) 螢光奈米鑽石對植物之顯像分析

- 1. 紅色螢光
 - (1). 藻體自體螢光顯像
 - A. 表皮細胞平面顯像

在共扼焦顯微鏡激發下,可發現本藻體之表皮自體螢光 極強,後經一平面掃描可得下【圖 29】,並得之其細胞發 光處位於表皮內。【圖 30】則顯示該捕蟲囊上被掃描之區 域(藍色線條)有著強烈的自體螢光。





B.捕蟲囊內生物體之強烈自體螢光

在捕蟲囊內,本組可在電腦上發現其中強烈的紅色螢光 團,會移動且有生命跡象,由此可知捕蟲囊為一區域提供 其餘生物共生,如【圖 31】所示。



C.捕蟲囊內消化器官~四爪線毛

在【註3】文獻中提及之四爪線毛在共扼焦顯微鏡顯像 下亦可顯影,如【圖32】所示。



(2). FND red 5 / / g/ml 之顯像結果

A. 紅色自體螢光強烈,透過顯微鏡下觀察並無法區別螢光奈 米鑽石與自體螢光差別,如【圖 33】所示。



B.表皮細胞單層顯色可看出其表層有不規則形狀,推測可能為奈米鑽石包覆或未成熟之捕蟲囊顯像,如【圖 33】所示。(3). FND red 100 µg/ml 之顯像結果



C. 在 FND 100 µg/ml 下之顯像可以反映表層明顯有一 層似片狀的覆蓋物,可推測該物即為奈米鑽石,如下 【圖 35】所示。



[\mathbb{B} 35] bladder traps' reflection in 100µg/ml's ND solution.

D. 即使有奈米鑽石包覆,亦可發現該囊中生物體仍存活。 相對於【圖 31】與【圖 32】,更可發現所有眼蟲有擴 散趨勢,下【圖 36】與上【圖 35】明顯可發現其擴 散與活動情形。



 $\mathbb{S} \equiv 36$]bladder traps' reflection in 100 μ g/ml's ND solution.

C.【圖 37】是尚未取後段光波之圖,物體與【圖 36】相同,故對照下可發現,所有生物紅色自體螢光都有相當的顯著性。



(4). FND 吸附特性介绍

就如同動機所述,本組從事重金屬吸附之題目來源, 即為本結果所影導,在【圖1】中可觀察出在莖上的螢 光奈米鑽石吸附粒子。



2.綠色螢光

- (1). 藻體自體螢光顯像
 - A. 表皮自體螢光顯像

在紅色螢光部分明顯了解植物藻體自體螢光之強度,但



如【圖 38】所示,其綠色螢光部分並無過強烈之處。

(二). 植株、奈米鑽石作用與吸附重金屬之量質分析、討論

1. 不同奈米鑽石吸附下之同量硝酸鉛溶液吸附狀況

(1). 實驗數據



(2). 實驗圖表



2.現象概述

- 從【表1】與【表2】中,本組可以強調其必有吸附重 a. 金屬梨子的功效。所有含植物的溶液中,暫不論其上 FND 含量,皆具有吸附功能,透過導電度,本組可清楚 了解吸附的重要指標。
- 對於不同濃度溶液下所產生的吸附,並無法發掘其明顯 b. 的規律性,故此實驗無法指出不同 ND 對吸附關係的影 壑。

(三)ND(尚未酸洗)與重金屬之共同放置反應(離心前)

1.外觀差異



(1) 0 minutes: 放入奈米鑽石初期,並不會有明顯差異。

【圖 39】 放入 ND (0 minutes) 白底



(2).10 minutes: 放入奈米鑽石十分鐘後,不同硝酸鉛 濃度的溶液開始可以觀察到差異,200ppm之硝酸鉛溶 液含最深之身色沉澱,其餘溶液隨硝酸鉛濃度減少, 黑色沉澱範圍逐漸縮小。上述如【圖 41】所示。



(3) 1 day

放置一天後,硝酸鉛濃度為200ppm之奈米鑽石溶液較【圖 41】之溶液而言,上方液體清澈度明顯提高,下方沉澱物也有 些許增加。至於100ppm,本組也可發現下方黑色沉澱物有增 加趨勢,上述如【圖42】所示



(13)

(4) 5days

放置五天後,可迅速分別出各濃度的差異,並可再次證明濃 度與沉澱量關係。隨著時間增加,亦可發現硝酸鉛溶液100ppm 的清澈度上升,此現象可證明時間與沉澱量或清澈度之連結, 如【圖43】所示。



- (5) 現象概述
 - A. 時間增加可增加溶液清澈度與沉澱量
 - B. 重金屬濃度越高,溶液上方液體越容易清澈。
 - C. 此現象可能來自重金屬與奈米鑽石的結合變重所致,須 看微觀來證明。
 - D. 因此批樣本只將其配製飽和某些沉澱現象是原本的奈米 鑽石,故用清澈度檢測較為精準。
- 2.導電率變化
- (1) 圖表與數據文字敘述

由【表 5】可得知放入奈米鑽石的確具減少導電度作用,但 見【表 6】、【表 9】和【表 12】時,導電率卻有不減反增的現 象。見【表 10】及此份奈米鑽石的特質可得知,因其為未酸 洗之批,故上面連接的官能基尚無法確定,或能提及裡面之物 體繁複。雖因無法確定之樣本來做此實驗並不能從導電度確定 其是否有吸收重金屬之效,但能提出一假設:裡面的組成成分 正在改變甚有大幅改變的趨勢,若透過先前所提及的沉澱現象 亦可證明導電度的假設是正確無誤的。

(2) 不同濃度下之分別比較

透過不同濃度下所記錄的圖表與數據觀察不同導電率下的

影響與差異。

I. 200 ppm



II. 100ppm

eooppin ee	umuate				twice															
details/t	me(min	ı)			0.5		1.0	1.5	5	2.0		2.5		3.0	3.5		4.0	4	1.5	5.0
	r	esistance	•			18.597	18	.585	18.57	8	18.300		18.034	18.02	29	17.251	1	6.997	16.769	17.003
		100																		
condu	ictivity to	r 100ppi	m Lead n	itrate	0.054	0.07.4	0.054	0.0	24	0.05	0.072	0.055	0.676	0.05	5 0.05	8	0.059	0 700	0.060	0.059
13.3-V TOF 1	uuppm Lea	id hitrate				0.654	10	662	0.66	/	0.673		0.676	10.68	10	0.707		3.722	0.723	0.718
						0.69	12	000	12.05	2	0.69	1	0.70	12.02	0	0.72	T	0.74	0.75	0.74
						0.00			0.0	,	0.05		0.70	0.7	0	0.75		0.74	0.75	0.74
5.5	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5	10.0	10.5	11.0	11.5	12	.0	12.5	13.0	13.5	14.0	14.5	15.0
16.997	16.532	16.529	9 16.53	4 16.0	86 16.07	7 16.765	5 16.537	16.077	15.447	15.44	7 15.054	15.03	9 14	.849	14.667	14.148	13.808	13.63	85 13.6	27 13.470
0.059	0.060	0.060	0.060	0.062	0.062	0.060	0.060	0.062	0.065	0.065	0.066	0.066	0.0	67	0.068	0.071	0.072	0.073	0.073	0.074
0.722	0.736	0.738	0.73	4 0.7	47 1.26	0 0.726	0.732	0.760	0.788	0.788	3 0.805	0.818	s 0.	.827	0.833	0.850	0.873	0.89	2 0.8	19 0.908
12.578	12.564	12.50	2 12.50	c 0.	4/ 12.5	P 0.75	4 12.568	12.54	12.512	12.51	2 12.49	0.93	2 12	.4/3	12.467	12.45	0.00	/ 12.40	1 00	1 12.39
0.74	0.76	0.76	0.71	ь U	0.7	8 0.75	0.76	0.78	0.81	0.81	L 0.83	0.83	. (J.84	0.85	0.88	0.90	0.9	1 0.5	0.92
15.5	16.0	16.5	170	175	18.0	18.5	19.0	195	20.0	20.5	21.0	21.5	22.0) 2	2.5	23.0	23.5	24.0	24.5	25.0
13.025	12.593	12.587	12.188	12.187	12.188	11.941	11.693	11.453	11.453	11.569	11.343	11.445	11.3	38 1	11.560	11.454	11.330	11.330	11.332	11.559
0.077	0.079	0.079	0.082	0.082	0.082	0.084	0.086	0.087	0.087	0.086	0.088	0.087	0.088	0.	.087	0.087	0.088	0.088	0.088	0.087
0.926	0.959	0.965	0.990	0.991	0.990	1.001	1.022	1.045	1.045	1.037	1.050	1.054	1.05	55	1.046	1.044	1.064	1.064	1.061	1.047
12.374	12.341	12.335	12.31	12.309	12.31	12.299	12.278	12.255	12.255	12.263	12.25	12.246	12.2	45 1	L2.254	12.256	12.236	12.236	12.239	12.253
0.95	0.98	0.98	1.01	1.01	1.01	1.03	1.05	1.07	1.07	1.06	1.08	1.07	1.0	8(1.06	1.07	1.08	1.08	1.08	1.06
25.5	26.0	26.	5 2	7.0	27.5	28.0	28.5	29.0	29.	5 3	0.0									
11.805	11.80	4 11.7	797 1	1.930	12,180	12.061	12.310	12.45	2 12.3	25 1	2.576									
0.085	0.085	0.08	5 01	084	0.082	0.083	0.081	0.080	0.08	1 0	080									
1.022	1.000	0.00	21 -	1 01 2	0.002	0.000	0.001	0.080	0.00	75 0.	0.076									
1.023	1.024	+ 1.0	121 1	1.012	0.998	0.998	0.990	0.97	5 0.9	/5	0.970									
12.277	12.27	b 12.2	269 1	2.288	12.302	12.302	12.31	12.32	/ 12.3	25 1	.2.324	-	0	•	Ŧ	1.1	~~		-L-I	1 5
1 0 4	1.0/	1	04	1.03	1 01	102	1.00	0.99	9 1	00	0.08	ΙŦ	ĸ		1 00	ылг	()()m	nm	1 世紀	· tF





0 ppm

	III.	50 ppm			
Oppm Lead nitrate letails/time(min)	0.5	1.0 1.5	2.0 2.5	3.0 3.5 4.0	4.5 5.0
resistance conductivity for 50ppm Lead nitr 3.3-V for 50ppm Lead nitrate	24.206 ate 0.041 0.471 12.829	24.685 25.173 0.041 0.040 0.464 0.462 12.836 12.838	25.706 25.11 0.039 0.040 0.447 0.45 12.853 12.84	24.681 24.189 0.041 0.041 0.042 3 0.466 0.480 7 12.834 12.820	23.731 23.282 22.846 0.043 0.044 0.485 0.495 0.506 12.815 12.805 12.734
5.5 6.0 6.5 7.0 22.423 22.028 21.632 20.8	0.53	0.52 0.51 8.5 9.0 9.5 10 21.634 21.258 20.189 19	0.50 0.5 0.0 10.5 11.0 1 1538 18.940 19.864 1	1 0.52 0.53 1.5 12.0 12.5 13. 19.866 19.859 18.635 18.3	0.54 0.55 0.56 0 13.5 14.0 14.5 15.0 43 18.641 19.532 19.545 19.529
0.045 0.045 0.046 0.048 0.519 0.524 0.537 0.55 12.781 12.776 12.763 12.7	0.048 0.047 0.553 0.547 48 12.747 12.753	0.046 0.047 0.050 0.0 0.536 0.545 0.581 0. 12.764 12.755 12.719	51 0.053 0.050 0. 600 0.610 0.587 12.7 12.69 12.713 1	050 0.050 0.054 0.05 0.586 0.590 0.628 0.6 .2.714 12.71 12.672 12.6	5 0.054 0.051 0.051 0.051 43 0.624 0.604 0.596 0.606 57 12.676 12.696 12.704 12.694
0.57 0.58 0.59 0.6 15.5 16.0 16.5 17.0 19.224 19.230 19.235 19.548	1 0.61 0.60 17.5 18.0 20.197 19.873	0.59 0.60 0.63 0 18.5 19.0 19.5 20 19.239 19.238 19.546 20	0.65 0.67 0.64 0.0 20.5 21.0 2 0.877 20.874 19.867	0.64 0.64 0.68 0. 21.5 22.0 22.5 23 19.551 19.552 20.529 20	69 0.68 0.65 0.65 0.65 .0 23.5 24.0 24.5 25.0 .195 20.195 19.560 19.239 19.560
0.052 0.052 0.052 0.051 0.612 0.608 0.605 0.594 12.688 12.692 12.695 12.706 0.66 0.66 0.66 0.65	0.050 0.050 0 0.576 0.581 12.724 12.719 0.63 0.64	0.052 0.052 0.051 0.0 0.602 0.603 0.595 0 12.698 12.697 12.705 12 0.66 0.66 0.65 12	148 0.048 0.050 0 1565 0.567 0.585 0.573 12.713 12.735 12.733 12.715 0.61 0.64	0.051 0.051 0.049 0.01 0.592 0.591 0.572 0. 12.708 12.709 12.728 12 0.65 0.65 0.62 0	0 0.050 0.051 0.052 0.051 577 0.577 0.586 0.602 0.586 723 12.723 12.714 12.698 12.714 0.63 0.65 0.66 0.65 0.65
25.5 26.0 26.5 27.0 20.885 22.026 22.019 21.245	27.5 28.0 28 20.552 20.544 20	3.5 29.0 29.5 30.0 0.907 20.561 20.539 20.537			
0.048 0.045 0.045 0.047 0.560 0.525 0.529 0.553 12.74 12.775 12.771 12.747 0.61 0.58 0.58 0.60	0.049 0.049 0.0 0.558 0.563 0 12.742 12.737 1: 0.62 0.62	448 0.049 0.049 0.049 .547 0.552 0.566 0.567 2.753 12.748 12.734 12.733 0.61 0.62 0.62 0.62	· 【主 0】Ⅰ	and 50mm t	赵坡
00.0 00.0 00.0	0.02 0.02	0.01 0.02 0.02 0.02			赵 1 家
Donly - 50ppm Lead nitrate etails/time(min)	1 day 0.5	1.0 1.5	2.0	2.5 3.0 3.5	4.0 4.5 5.0
resistance conductivity for 50ppm Lead ni	trate ND 0.072	13.823 13.502 0.074 0.076	13.188 12.756 5 0.078	12.478 12.209 0.080 0.082 0.08	11.835 11.591 11.362 11.2 4 0.086 0.088 0.089
3.3-V for 50ppm Lead nitrate ND		12.441 12.422 0.900 0.920 0.859 0.878	12.397 12.373 0.940 0.97 0.903 0.927	12.353 12.331 0.990 1.010 0.947 0.969	12.308 12.286 12.271 12.2 1.040 1.06 1.08 1.1 0.992 1.014 1.029 1.04
5.5 6.0 6.5 7.0 11.128 10.914 10.912 10.8	7.5 8.0	8.5 9.0 9.5 2 10.402 10.304 10.036	10.0 10.5 11.0 10.023 9.840 9.751	11.5 12.0 12.5 9.504 9.344 9.258	13.0 13.5 14.0 14.5 15.0 9.105 8.955 8.811 8.449 8.59
0.090 0.092 0.092 0.09 12.241 12.224 12.221 12.2	3 0.093 0.095 09 12.196 12.187	0.096 0.097 0.100 (12.17 12.159 12.143	0.100 0.102 0.103 12.128 12.103 12.091	0.105 0.107 0.108	0.110 0.112 0.113 0.118 0.116 12.019 12 11.983 11.66 11.94
1.1 1.12 1.12 1 1.059 1.076 1.079 1.0 15.5 16.0 16.5 17.0	13 1.14 1.16 91 1.104 1.113 17.5 18.0	1.17 1.18 1.21 1.130 1.141 1.157 18.5 19.0 19.5 2	1.21 1.23 1.24 1.172 1.197 1.209 20.0 20.5 21.0	1.27 1.29 1.3 1.230 1.246 1.264 21.5 22.0 22.5 2	1.32 1.34 1.36 1.38 1.3 1.281 1.300 1.317 1.640 1.35 23.0 23.5 24.0 24.5 25.0
8.397 8.324 8.259 8.137 0.119 0.120 0.121 0.123	8.018 7.952	7.836 7.775 7.713	7.605 7.546 7.495	7.490 7.386 7.387 0.134 0.135 0.135 (7.385 7.336 7.285 7.228 7.227
11.924 11.904 11.893 11.88 1.42 1.43 1.44 1.46	0.123 0.123 3 11.866 11.849 5 1.48 1.49	11.832 11.818 11.801 1 1.51 1.52 1.53	11.787 11.772 11.767 1.55 1.56 1.57	11.76 11.743 11.745 1.57 1.59 1.59	11.742 11.738 11.729 11.71 11.701 1.59 1.6 1.61 1.62 1.61
1.376 1.396 1.407 1.420 25.5 26.0 26.5 27.0	1.434 1.451 0 27.5 28.0	1.468 1.482 1.499 28.5 29.0 29.5	30.0	1.540 1.557 1.555	1.228 1.262 1.271 1.240 1.242
7.127 7.078 6.987 6.93 0.140 0.141 0.143 0.144	39 6.937 6.939 0.144 0.144	6.895 6.895 6.938 0.145 0.145 0.144	6.939 0.144		
11.689 11.679 11.668 11.6 1.64 1.65 1.67 1. 1.611 1.621 1.632 1.64	57 11.654 11.657 68 1.68 1.68 13 1.646 1.643	11.653 11.653 11.656 1.69 1.69 1.68 1.647 1.647 1.644	11.657 1.68 1.643 【 丰 10	Lead 50nnn	n 淮 NID(丰酸洪)對
					I
1/Ω		50 ppm Lead r	nitrate		
1/Ω 0.160 0.140		50 ppm Lead r	nitrate		【表 11】
1/Ω 0.160		50 ppm Lead r	nitrate		【表 11】 50ppm Lead ND
1/Ω 0.160 0.140 0.120 0.100 0.080 0.060		50 ppm Lead r	nitrate		【表 11】 50ppm Lead ND and No
1/Ω 0.160 0.140 0.120 0.100 0.080 0.060 0.040		50 ppm Lead r	nitrate		【表 11】 50ppm Lead ND and No ND's
1/Ω 0.160 0.140 0.120 0.100 0.080 0.060 0.040 0.020 0.000 1<3	5 7 9 111315	50 ppm Lead r	nitrate	495153555759 pe	【表 11】 50ppm Lead ND and No ND's r 0.5 comparison

-conductivity for 50ppm Lead nitrate ND

etails/1	ime(mi	n)			0.5		1.0		1.5		2.0		2.5	3	3.0 3.	5	4.0	4	1.5	5.0
		resistanc	e			14.345		14.0	004	13.66	В	13.357		13.049	2.759	12.478	1	12.088	11.951	11.701
		ND only			0.070		0.071		0.07	3	0.075		0.077	(.078 0.0	180	0.083	C	0.084 (0.085
						12.480		12.4	64	12.438	3	12.422	1	2.397 1	2.376	12.353		12.33	12.31	12.286
						0.870		0.8	90	0.910)	0.93		0.950	0.970	0.990		1.02	1.03	1.05
3.3-V for	ontrol (N) METAL) I	ND			0.820		0.8	36	0.862	2	0.878		0.903	0.924	0.947		0.970	0.990	1.014
5.5	6.0	6.5	7.0	7.5	8.0	8.5	9	.0	9.5	10.0	10.5	11.0	11.5	12.0	12.5	13.0	13.5	14.0	14.5	15.0
11.244	11.02	0 10.80	5 10.419	0 10.22	9 10.1	20 9.8	53	9.592	8.618	7.840	7.605	7.333	6.985	6.79	6.537	6.413	6.290	6.173	3 6.092	6.006
0.000	0.001	0.000	0.000	0.000	0.000	0.10	0	104	0.110	0.1.20	0.1.21	0.120	0142	0147	0152	0150	0.150	0.162	0.104	0.100
0.089	0.091	0.093	0.096	0.098	0.099	0.10	10 1	2006	0.116	0.128	0.131	0.136	0.143	0.147	0.153	0.156	0.159	0.162	0.164	0.166
12.25	D 12.23	2 12.2	1 12.1	9 12.17	2 12.1	44 IZ.I	73 I	1.26	11.204	1 5 1	11./00	11./32	11.00	0 11.02 7 1.7	0 11.5/ 1 1.7	11.545	11.51	11.48	2 11.455 6 1.00	11.412
1.04	1.061	1 1.1	5 1.1 0 1.110	1126	, 119 119		20	1.20	2.096	1.51	1.55	1569	1625	1.67/	1 720	1 757	1 700	1 9 1 9	0 1.00	1.9
1.044	1.00	1.05		. 1.120	, 1.1.			1.2.14	2.050	1.401	1.512	1.500	1.055	1.07-	1.750	1.757	1.750	1.010	5 1.047	1.000
15.5	16.0	16.5	17.0	17.5	18.0	18.5	19	9.0	19.5	20.0	20.5	21.0	21.5	22.0	22.5	23.0	23.5	24.0	24.5	25.0
5.864	5.684	5.558	5.321	5.177	5.091	5.0)6 4	4.924	4.826	4.750	4.675	4.624	4.555	4.509	4.463	4.438	4.397	4.356	6 4.313	4.272
0.171	0.176	0.180	0.188	0.193	0.196	0.200	0.2	203	0.207	0.211	0.214	0.216	0.220	0.222	0.224	0.225	0.227	0.230	0.232	0.234
11.376	11.312	11.283	11.227	11.182	11.149	11.1	14 13	1.079	11.051	11.019	10.986	10.958	10.931	10.91	10.89	10.872	10.86	10.846	5 10.825	10.809
1.94	1.99	2.03	2.11	2.16	2.19	2.	22	2.25	2.29	2.32	2.35	2.37	2.4	2.42	2.44	2.45	2.47	2.49	9 2.51	2.53
1.924	1.988	2.017	2.073	2.118	2.151	2.18	6 2	.221	2.249	2.281	2.314	2.342	2.369	2.389	2.410	2.428	2.440	2.454	2.475	2.491
25.5	26.0	26.5	27.0 2	27.5 2	8.0	28.5	29.0	29.5	30.0											
4.250	4.230	4.208	4.166	4.164	4.142	4.140	4.139	4.12	2 4.12	0										
0.235	0.236	0.238	0.240 C	.240 0	241 (0.242 (.242	0.243	0.243											
10.796	10.786	10.772	10.748	10.743	L0.727	10.723	10.719	10.71	.6 10.71	.3										
2.54	2.55	2.56	2.58	2.58	2.59	2.59	2.59	2	.6 2.	.6	+ 1		т	1.0		بطر	15			
										-	-						THE			



(四) ND(尚未酸洗)與重金屬之共同放置反應(離心後)

經討論,本組認為若為奈米鑽石本身造成導電度變化則透過離心方 式讓處於懸浮狀態的<u>奈米粒子沉降(</u>註1)再進行導電率分析即可得到吸 附重金屬與否的數據。

註 1:如研究步驟 5.所述,因純粹為 ND 飽和溶液的樣本,離心後上方溶液仍呈白色混濁,故不做導電率比較。

1. 導電度比較

(1) 個別數據

ND only - 200p	opm Lead nit	rate		5 days	р	recipitates	centrifug	gation									
details/tim	e(min)			0.5		1.0	1.5		2.0	2.5		3.0	3.5	4.0		4.5	5.0
	resist	ance			10.304	10.0	20	9.845	9.751		9.498	9.255	9.097		8.875	8.736	8.525
conductivity	for 200pp	m Lead nit	rate ND Ce	n 0.097		0.100	0102		0.103	0.105		0.108	0.110	0113		0114	0117
13 3-V for 200	nom Lead nit	trate ND		0.057	1 1 4 1	115	76	1 1 9 1	1 209	0.205	1 2 3 8	1 268	1 292	0.115	1 3 1 9	1 331	1 365
V	ppin Lead in	and the			12.159	12.12	24	12.109	12.091		12.062	12.032	12.008		11.981	11.969	11.935
I					1.18	1.2	21	1.23	1.24		1.27	1.30	1.32		1.35	1.37	1.40
5.5	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5	10.0								
8.329	8.137	8.069	8.066	7.945	7.831	7.830	7.771	7.769	7.655								
0.120	0.123	0.124	0.124	0.126	0.128	0.128	0.129	0.129	0.131								
1.390	1.420	1.439	1.443	1.462	1.475	1.476	1.488	1.491	1.511								
11.91	11.88	11.861	11.857	11.838	11.825	11.824	11.812	11.809	11.789								
1.43	1.46	1.47	1.47	1.49	1.51	1.51	1.52	1.52	1.54	【去	15	I I	ead 20)() nr	hm	ND.	.cen)
										1	. 10		2	vohł	7111		conj

ND only - 100p	pm Lead nit	rate		5 days	c	entrifugation										
details/tim	e(min)			0.5		1.0	1.5		2.0	2.5		3.0	3.5	4.0	4.5	5.0
	resist	ance			8.624	8.4	53	8.230	8.005		7.727	7.504	7.281	7.145	7.002	6.964
conductivity	for 100pp	m Load nit	rate ND C	0.116		0.119	0122		0.125	0.120		0.122	0.127	0.140	0.142	0.144
I	101 100pp	in Leau Int	rate ND Co	0.110	1.382	1.4	0.122	1.441	1.477	0.125	1.524	1.564	1.606	1.633	1.662	1.670
V					11.918	11.8	93	11.859	11.823	1	11.776	11.736	11.694	11.667	11.638	11.63
5.5	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5	10.0							
6.856	6.710	6.596	6.455	6.324	6.193	6.007	5.938	5.856	5.775							
0.146	0.149	0.152	0.155	0.158	0.161	0.166	0.168	0.171	0.173							
1.693	1.725	1.751	1.784	1.816	1.849	1.898	1.917	1.940	1.963							
11.607	11.575	11.549	11.516	11.484	11.451	11.402	11.383	11.36	11.337	【表	16	L	ead 10)0ppm	(ND-	-cen)

ID only - 50p	pm Lead nitr	ate		5 days		entrifugatio	n										
letails/tin	ne(min)			0.5		1.0	1.5		2.0	2.5		3.0	3.5	4.0		4.5	5.0
	resis	tance			12.642	1:	2.358	11.950	11.409		11.124	10.909	10.498	1	10.213	10.024	9.7
conductivi	ty for 50pp	m Lead nit	rate ND c	en 0.079		0.081	0.08	34	0.088	0.090		0.092	0.095	0.098		0.100	0.102
					12.389	12	.358	12.308	12.208	1	L2.236	12.218	12.178	1	L2.154	12.129	12.1
					0.980	1	.000	1.030	1.07		1.100	1.120	1.160		1.19	1.21	1.
3.3-V for 50p	pm Lead nit	rate ND			0.911	C	1.942	0.992	1.092		1.064	1.082	1.122		1.146	1.171	1.1
3.3-V for 50p	opm Lead nit	rate ND 6.5	7.0	7.5	0.911	8.5	9.0	0.992	1.092		1.064	1.082	1.122		1.146	1.171	1.1
3.3-V for 50p 5.5 9.509	6.0 9.421	6.5 9.176	7.0 8.809	7.5 8.534	0.911 8.0 8.329	8.5 8.069	9.942 9.0 7.828	0.992 9.5 7.550	1.092 10.0 7.382		1.064	1.082	1.122		1.146	1.171	1.1
3.3-V for 50p 5.5 9.509	9.421	6.5 9.176	7.0 8.809	7.5 8.534	0.911 8.0 8.329	8.5 8.069	9.0 9.0 7.828	0.992 9.5 7.550	1.092 10.0 7.382		1.064	1.082	1.122		1.146	1.171	1.1
3.3-V for 50; 5.5 9.509 0.105	0.106	6.5 9.176 0.109	7.0 8.809 0.114	7.5 8.534 0.117	0.911 8.0 8.329 0.120	8.5 8.069 0.124	9.0 9.0 7.828 0.128	0.992 9.5 7.550 0.132	1.092 10.0 7.382 0.135		1.064	1.082	1.122		1.146	1.171	1.1
3.3-V for 50p 5.5 9.509 0.105 12.076	0.106 12.059	6.5 9.176 0.109 12.021	7.0 8.809 0.114 11.98	7.5 8.534 0.117 11.947	0.911 8.0 8.329 0.120 11.91	8.5 8.069 0.124 11.861	9.0 7.828 0.128 11.82	0.992 9.5 7.550 0.132 11.778	1.092 10.0 7.382 0.135 11.737		1.064	1.082	1.122		1.146	1.171	1.1
3.3-V for 50p 5.5 9.509 0.105 12.076 1.27	0.106 12.059 1.28	6.5 9.176 0.109 12.021 1.31	7.0 8.809 0.114 11.98 1.36	7.5 8.534 0.117 11.947 1.4	0.911 8.0 8.329 0.120 11.91 1.43	8.5 8.069 0.124 11.861 1.47	9.0 7.828 0.128 11.82 1.51	0.992 9.5 7.550 0.132 11.778 1.56	1.092 10.0 7.382 0.135 11.737 1.59		1.064	1.082	1.122		1.146	1.171	1.1

(2) 比較圖表



(3) 文字概述

對於上述圖表尤其是【表 19】、【表 21】所示,本組可更加 確定奈米鑽石並無提升整體導電度之效,或可解釋為奈米鑽 石尚無確切的導電性,【表 22】甚顯出樣本較奈米鑽石溶液導 電度高的反應,而增加整體導電度應是未酸洗之奈米鑽石上 吸附的其他官能基,可是奈米鑽石為交換樹脂。至於其吸附 結構與平面顯影則需透過 XRD、TEM 與 SEM 來檢測,而此 方面將於酸洗後的奈米鑽石實驗中提及並介紹不同重金屬離 子與奈米鑽石的吸附情形。

(五) ND(酸洗後之奈米鑽石 ND-COOH)吸附重金屬外觀、導電度、結構與表面顯像

1.肉眼觀察 (1) 硝酸鉛



(2) 硝酸鎳



(3) 硝酸锌



(3) 觀察概述

此批樣本沉澱較為乾淨,上方溶液溶液清澈,應為此次實驗 有固定奈米鑽石量(約為 500~1000 µg/ml)所保持。

- 2.SEM 下樣本微觀
 - (1) 硝酸鉛

A. 微觀分析





B. 文字敘述

從紅色圓圈所框出之處有明顯的小型沉澱聚集,並 且尚有較多三角扇形沉澱,小型鑽石主要聚於扇形邊 緣居多,其餘皆附著於其餘形狀內。黃色圓圈所圈出 範圍,最能見其大型聚集狀況,固可先推測重金屬離 子確實有聚集功能。

C. 元素分析



【表 22】 Lead 600nm scale range

0 2 Full Scale 3292 cts	4 6 8 Cursor: 0.000	3 10 12	Shettron 7 Spectrum 2 14 te		and the second second
Element	Weight%	Atomic%			
C K	97.18	97.87			
O K	2.82	2.13			
Totals	100.00		Sec. 5		
			1µm	Electron Image 1	

- 【表 23】 Lead 1 μ m scale range
- 此數據顯示不論間距大小 C, O 比例相似。
- b. 並無 Pb 以元素狀態呈現。

a.

(2). 硝酸鋅 A. 微觀分析



【圖 52】	
Zn(NO ₃) ₂ SEM	
100000*	



【圖 53】 Zn(NO₃)₂ SEM 150000*



【圖 54】 Zn(NO₃)₂ SEM 50000*

B. 文字敘述

從紅色圈出處可發現有許多小型奈米鑽石附著於 其他大型奈米鑽石上。而耐名鑽石得形狀亦不像 Pb 的扇形相似。大型沉聚少,小型附著顯著為多。







- 1. Zn 有元素狀態,應是 ZnO
- 2. Zn 的比例不因不同尺度而有所改變。

(3). 硝酸鎳 A. 微觀分析


B.文字敘述

在硝酸鎳的圖像中,可針對其吸附顆粒大小作分析, 經本組觀察可發現紅色框處尚有許多較為大型沉澱 (由小沉澱聚合而成),其餘多為大型沉澱互相吸引。

C.元素分析

0 2	4 6 8	10 12	Spectrum 5	1. 2. 2.
Full Scale 3292 cts U	ursor: 0.000		ke∀	
Element	Weight%	Atomic%	ke∀ -	
Element C K	Weight% 97.63	Atomic% 98.21	ke∨	N.C.S.
Element C K O K	Weight% 97.63 2.37	Atomic% 98.21 1.79	keV	A RECENT



Electron Image 1

【表 26】 Nickel 600nm scale range



a.數據顯示 C、O 比例不因範圍而異。 b.與其他元素所做比例相似。 (4).互相比較



且鉛的聚集較為明顯,其餘離子可到結論(六)1.(3)微觀分析進行對 照與探討。

3. 導電度測量

(1) 硝酸鉛導電數據與曲線

ND(-COOH)	- 200ppm	Lead nitrat	te		1.5 days																
details/ti	me(mir	1)			0.5		L.O	1.5	5	2.0		2.5		3.0	3.5		4.0		4.5	5.0)
	r	esistance				14.549	14.	200	14.02	20	13.530	1	2.931	12.645	12	.242	1:	2.114	11.6	15	11.273
onductivity	/ for 200p	opm Lead	nitrate N	ID(-COOI	0.069		0.070	0.07	71	0.074		0.077		0.079	0.082		0.083		0.086	0.01	39
V						12.512	12.4	196	12.47	8	12.448	1.	2.414	12.392	12	364	1	2.356	12.3	12	L2.288
1221/42	00					0.860	0.0	580	0.89	0	0.92		0.960	0.980	1	010		1.02	1.	06	1.09
13.3-V TOP 21	ooppm Lea	su nitrate N	ID(-COOH)			0.788	0.0	504	0.82	2	0.852		1.886	0.908	0	930	(1.944	0.98	00	1.012
E E	6.0	6 5	7.0	75	٥ n	0 E	9.0	0.5	10.0	105	11.0	11 5	12	0 1) E 1	2 0	12 E	1/	0	1/5	15.0
11 268	11 159	10.835	10.629	10.630	10 624	10.628	10.928	10,931	10.929	10.828	10.63	10.531	10.4	428 1	0.330	0.242	10 237	7 10	142	10 238	10.332
		10.000	10.020	10.000	10.024	10.020	10.020	10.001	10.020	10.020	10.000	. 10.001	.0.				10.207	10		. 5.200	10.002
0.089	0.090	0.092	0.094	0.094	0.094	0.094	0.092	0.091	0.091	0.092	0.094	0.095	0.09	6 0.	097 0	098	0.098	0.0	99 (0.098	0.097
12.282	12.275	12.243	12.223	12.225	12.218	12.222	12.239	12.243	12.241	12.236	12.22	4 12.210	5 12.2	201 1	2.189	2.188	12.18	2 1	2.17	12.183	12.192
1.09	1.1	1.13	1.15	1.15	1.15	1.15	1.12	1.12	1.12	1.13	1.1	5 1.10	5 1		1.18	1.19	1.19	9	1.2	1.19	1.18
1.018	1.025	1.057	1.077	1.075	1.082	1.078	1.061	1.057	1.059	1.064	1.076	5 1.084	1.0	99 3		1.112	1.118	1.	130	1.117	1.108
15.5	16.0	16.5	170 '	175 1	180 1	25	19.0	105	20.0	20.5	21.0	21.5	22.0	22.5	23.0	2:	25 3	24.0	2/15	25	0
10.245	10.243	10.327	10.329	10.241	10.332	10.335	10.429	10.533	10 731	10.630	10.428	10 240	10 144	9.88	0 970	2	9 616	9.530	9.4	46 9	363
0.098	0.098	0.097	0.097 (0.098 0	0.097 0	.097	0.096	0.095	0.093	0.094 (0.096	0.098	0.099	0.101	0.103	0.1	L04 0	.105	0.106	0.10)7
12.191	12.189	12.186	12.188	12.187	12.192	12.195	12.202	12.218	12.233	12.225	12.201	12.186	12.173	12.15	2 12.12	7 1	2.116	12.103	12.0	91 12	078
1.19	1.19	1.18	1.18	1.19	1.18	1.18	1.17	1.16	1.14	1.15	1.17	1.19	1.2	1.2	3 1.2	5	1.26	1.27	1.	28	1.29
1.109	1.111	1.114	1.112	1.113	1.108	1.105	1.098	1.082	1.067	1.075	1.099	1.114	1.127	1.14	3 1.17	3 1	.184	1.197	1.20	9 1.	222
25.5	26.0 2	26.5 2	7.0 27	7.5 28	.0 28.	5 29.	29.5	30.0													
9.203	9.038	9.035	8.956 8	8.952 8	.949 8.4	876 8.8	02 8.72	7 8.65	4												
0.109 (0.111 0	0.111 0.	112 0.1	.12 0.1	12 0.11	3 0.11	\$ 0.115	0.116	1												
12.056	12.021	12.016 1	2.001 11	1.996 11	.991 11.	982 11.9	26 12	6 11.94	13												
1.31	1.55	1.33	1.34 1.299 1	1.34 304 1	1.54] 309 13		.50 1.3 29 1.24	4 125	7 7	± 20	т	and	200			+h	ND	C	\sim	тт	
1.244	1.215	1.204	1.2.3.5 1		505 1.5	10 1.5	2.5 1.54	- 1.55		衣 28	L	lead	200	ppi	n W	ın	IND	-0	50	н	

etails/ti	ime(mir	1)			0.5	1	L.O	1.	5	2.0		2.5	3.0	3.5		4.0	4.5	5.)
	r	esistance	9			39.545	39.	530	39.54	5	38.326	36	.153 37.	189	37.203	37.	229 36	.136	36.142
ductivity	ofor 100r		l nitrato l		0.025		0.25	0.0	25	0.026		0.028	0.0	27 0.02	7	0.027	0.02	2 00	20
uuctivity	101 100	philead	initiatei	VD(-COO	0.025	12.050	121	0.0	12.05	0.020	12 021	12	015 120	16	12 021	0.027	0.02	000	12.011
						0330	13.	330	0.33	5	0 34	10	360 03	50	0.350	1.	135	036	036
8.3-V for 1	00ppm Lea	ad nitrate I	ND(-COOH)		0.250	0.3	255	0.25	5	0.269	0	285 0.2	84	0.279	0.2	270 0	291	0.289
5.5	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5	10.0	10.5	11.0	11.5	12.0	12.5	13.0	13.5	14.0	14.5	15.0
36.144	36.139	37.203	37.200	36.150	36.136	36.133	36.131	36.136	36.150	36.147	36.142	36.153	36.150	36.147	36.142	37.203	37.214	37.217	37.229
0.028	0.028	0.027	0.027	0.028	0.028	0.028	0.028	0.028	0.028	0.028	0.028	0.028	0.028	0.028	0.028	0.027	0.027	0.027	0.027
13.012	13.01	13.021	13.02	13.014	13.009	13.008	13.007	13.009	13.014	13.013	13.011	13.015	13.014	13.013	13.011	13.021	13.025	13.026	13.03
0.36	0.36	0.35	5 0.35	0.36	0.36	0.36	0.36	0.36	0.36	0.36	0.36	0.36	0.36	0.36	0.36	0.35	0.35	0.35	0.35
0.288	0.290	0.279	0.280	0.286	0.291	0.292	0.293	0.291	0.286	0.287	0.289	0.285	0.286	0.287	0.289	0.279	0.275	0.274	0.270
.5.5	16.0	16.5	17.0	17.5	18.0	18.5	19.0	19.5	20.0	20.5	21.0	21.5	22.0	22.5	23.0	23.5	24.0	24.5	25.0
30.320	30.329	30.333	30.330	30.344	30.347	39.316	30.330	30.344	0.330	30.332	30.321	9 30.334	30.344	30.330	39.516	39.321	39.327	39.53	39.55
0.026	0.026	0.026	0.026	0.026	0.026	0.025	0.026	0.026	0.026	0.026	0.026	0.026	0.026	0.026	0.025	0.025	0.025	0.025	0.025
13.031	13.032	13.034	13.035	13.037	13.038	13.041	13.039	13.03	7 13.035	13.033	13.03	2 13.0334	13.03	13.039	13.041	13.042	13.044	13.04	5 13.04
0.34	0.34	0.34	0.34	0.34	0.34	0.33	0.34	0.34	4 0.34	0.34	0.3	4 0.34	+ 0.34	0.34	0.33	0.33	0.33	0.3	8 0.3
0.269	0.268	0.266	0.265	0.263	0.262	0.259	0.261	0.263	0.265	0.267	0.268	0.267	0.263	0.261	0.259	0.258	0.256	0.255	0.25
25.5	26.0	26.5	27.0	27.5	28.0	28.5	29.0	29.5	30.0										
39.542	39.548	40.791	40.797	40.800	40.806	40.809	40.816	42.139	42.142										
	0.005	0.005	0.005	0.005	0.005	0.005	0.005												
12.040	12.051	12.052	12.055	12.056	12.059	12.050	12.061	12.062	12.064										
13:045	12:021	12:022	12:032	12:030	12:038	12:023	10.001	15.003	15.004										
0.55	0.35	0.32	0.32	0.32	0.32	0.32	0.32	0.237	0.236	Γ±	. 20	1 T /	hee	1000	nm	with	ND	CC	ΩЦ
0.2.31	0.245	0.247	0.245	0.244	0.242	0.241	0.200	0.207	0.200	【衣	29		Jau	τυυμ	pm	witti		-00	ЮП



(2) 硝酸鎳導電數據與曲線

stails/t					1.5 days		~								_	1.0			
. cuirs, c	ime(mii	1)			0.5	1	0	1.5		2.0	2	2.5	3.0	3.5		4.0	4.5	5.0	
	r	esistance	9			7.187	7.1	40	7.136		7.139	7.1	87 7.13	5	7.135	7.09	91 7.	135	7.089
uctivity	for 200n	nm Nick	el nitrate	ND(-COC	0139	0	140	0.140)	0 1 4 0	0	139	0 1 4 0	0 1 4 0		0 1 4 1	0 140	0.14	1
activity	101 2000	piniticit			0.155	1.715	11.7	10	11.703	0.110	11.708	11.71	.5 11.703	3	11.702	11	1.7 11	701 1	1.697
						1.630	1.6-	40	1.640		1.64	1.63	0 1.640)	1.640	1.	65 3	L.64	1.65
.3-V for 2	00ppm Ni	ckel nitrate	ND(-COO	H)		1.585	1.5	90	1.597		1.592	1.58	1.597	7	1.598	1.60	00 1.5	599 1	.603
5.5	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5	10.0	10.5	11.0	11.5	12.0	12.5	13.0	13.5	14.0	14.5	15.0
7.088	7.085	5 7.04	0 7.039	7.037	7.036	6.991	6.989	6.988	6.987	6.943	6.942	6.940	6.938	6.935	6.893	6.888	6.883	6.842	6.8
.141	0.141	0.142	0.142	0.142	0.142	0.143	0.143	0.143	0.143	0.144	0.144	0.144	0.144	0.144	0.145	0.145	0.145	0.146	0.146
11.695	5 11.69	1 11.68	7 11.68	5 11.681	L 11.679	11.675	11.672	11.67	11.668	11.665	11.6625	11.66	11.656	11.65	11.649	11.641	11.632	11.631	11.6
1.65	5 1.6	5 1.6	6 1.6	6 1.66	5 1.66	1.67	1.67	1.67	1.67	1.68	1.68	1.68	1.68	1.68	1.69	1.69	1.69	1.7	
1.605	1.609	1.613	1.615	1.619	1.621	1.625	1.628	1.630	1.632	1.635	1.638	1.640	1.644	1.650	1.651	1.659	1.668	1.669	1.6
L5.5	16.0	16.5	17.0	17.5	18.0	185	19.0	195	20.0	20.5	21.0	21.5	22.0	00.5				245	25
6.838	6.838	6.791	6.789	6.785	6.739	6.692	6.603	6.556	6.508	6.503	6.462	6.460	6.420	22.5 6.415	23.0 6.373	23.5 6.368	24.0 6.366	6.364	6
6.838	6.838	6.791	6.789	6.785	6.739	6.692	6.603	6.556	6.508	6.503	6.462	6.460	6.420	6.415	23.0 6.373	23.5 6.368	24.0 6.366	6.364	6
6.838 0.146	6.838 0.146	6.791 0.147	6.789 0.147	6.785 0.147	6.739 0.148	6.692 0.149	6.603 0.151	6.556 0.153	6.508 0.154	6.503 0.154	6.462 0.155	6.460 0.155	6.420 0.156	6.415 0.156	23.0 6.373 0.157	23.5 6.368 0.157	24.0 6.366 0.157	6.364 0.157	6 0.1
6.838 0.146 11.625	6.838 0.146 11.624	6.791 0.147 11.613	6.789 0.147 11.61	6.785 0.147 11.603	6.739 0.148 11.591	6.692 0.149 11.578	6.603 0.151 11.556	6.556 0.153 11.538	6.508 0.154 11.519	6.503 0.154 11.511	6.462 0.155 11.502	6.460 0.155 11.498	6.420 0.156 11.491	0.156 11.482	23.0 6.373 0.157 11.47	23.5 3 6.368 0.157 1 11.462	24.0 6.366 0.157 11.458	6.364 0.157 11.455	0.1 11
6.838 0.146 11.625 1.7	6.838 0.146 11.624 1.7	6.791 0.147 11.613 1.71	6.789 0.147 11.61 1.71	6.785 0.147 11.603 1.71	6.739 0.148 11.591 1.72	6.692 0.149 11.578 1.73	6.603 0.151 11.556 1.75	6.556 0.153 11.538 1.76	6.508 0.154 11.519 1.77	6.503 0.154 11.511 1.77	6.462 0.155 11.502 1.78	6.460 0.155 11.498 1.78	6.420 0.156 11.491 1.79	0.156 11.482 1.79	23.0 6.373 0.157 11.47 1.1	23.5 3 6.368 0.157 1 11.462 8 1.8	24.0 6.366 0.157 11.458 1.8	0.157 0.157 11.455 1.8	0.1 11
6.838 0.146 11.625 1.7 1.675	6.838 0.146 11.624 1.7 1.676	6.791 0.147 11.613 1.71 1.687	6.789 0.147 11.61 1.71 1.690	6.785 0.147 11.603 1.71 1.697	6.739 0.148 11.591 1.72 1.709	6.692 0.149 11.578 1.73 1.722	6.603 0.151 11.556 1.75 1.744	6.556 0.153 11.538 1.76 1.762	6.508 0.154 11.519 1.77 1.781	6.503 0.154 11.511 1.77 1.789	6.462 0.155 11.502 1.78 1.798	6.460 0.155 11.498 1.78 1.802	0.156 11.491 1.79 1.809	0.156 11.482 1.79 1.818	23.0 6.373 0.157 11.47 1.829	23.5 6.368 0.157 1 11.462 8 1.8 1.838	24.0 6.366 0.157 11.458 1.8 1.842	0.157 6.364 0.157 11.455 1.8 1.845	0.1 11
6.838 0.146 11.625 1.7 1.675	6.838 0.146 11.624 1.7 1.676	6.791 0.147 11.613 1.71 1.687	6.789 0.147 11.61 1.71 1.690	6.785 0.147 11.603 1.71 1.697	6.739 0.148 11.591 1.72 1.709	6.692 0.149 11.578 1.73 1.722	6.603 0.151 11.556 1.75 1.744	6.556 0.153 11.538 1.76 1.762	6.508 0.154 11.519 1.77 1.781	6.503 0.154 11.511 1.77 1.789	6.462 0.155 11.502 1.78 1.798	6.460 0.155 11.498 1.78 1.802	0.156 11.491 1.79 1.809	0.156 11.482 1.79 1.818	23.0 6.373 0.157 11.47 1.829	23.5 6.368 0.157 1 11.462 8 1.8 1.838	24.0 6.366 0.157 11.458 1.8 1.842	0.157 11.455 1.8 1.845	0.1 11
6.838 1.146 11.625 1.7 1.675	6.838 0.146 11.624 1.7 1.676	6.791 0.147 11.613 1.71 1.687 26.5	6.789 0.147 11.61 1.71 1.690	6.785 0.147 11.603 1.71 1.697 7.5 28	6.739 0.148 11.591 1.72 1.709	6.692 0.149 11.578 1.73 1.722	6.603 0.151 11.556 1.75 1.744	6.556 0.153 11.538 1.76 1.762	6.508 0.154 11.519 1.77 1.781	0.154 11.511 1.77 1.789	6.462 0.155 11.502 1.78 1.798	6.460 0.155 11.498 1.78 1.802	0.156 11.491 1.79 1.809	22.5 6.415 0.156 11.482 1.79 1.818	23.0 6.373 0.157 11.47 1.4 1.829	23.5 6.368 0.157 1 11.462 8 1.8 1.838	24.0 6.366 0.157 11.458 1.8 1.842	24.3 6.364 0.157 11.455 1.8 1.845	0.1 11
6.838 0.146 11.625 1.7 1.675 5.5 6.319	6.838 0.146 11.624 1.7 1.676 26.0 6.278	6.791 0.147 11.613 1.71 1.687 26.5 6.236	6.789 0.147 11.61 1.71 1.690 7.0 2 6.231	6.785 0.147 11.603 1.71 1.697 7.5 28 6.194 6	6.739 0.148 11.591 1.72 1.709 0 28.5 152 6.1	6.692 0.149 11.578 1.73 1.722 29.0 49 6.11	6.603 0.151 11.556 1.75 1.744 29.5 3 6.110	6.556 0.153 11.538 1.76 1.762 30.0 6.074	6.508 0.154 11.519 1.77 1.781	0.154 11.511 1.77 1.789	6.462 0.155 11.502 1.78 1.798	6.460 0.155 11.498 1.78 1.802	0.156 11.491 1.79 1.809	22.5 6.415 0.156 11.482 1.79 1.818	0.157 11.47 1.829	23.5 6.368 0.157 1 11.462 8 1.8 9 1.838	24.0 6.366 0.157 11.458 1.842	0.157 6.364 0.157 11.455 1.845	0.1 11
6.838 0.146 11.625 1.7 1.675 6.319	6.838 0.146 11.624 1.7 1.676 26.0 6.278	6.791 0.147 11.613 1.71 1.687 26.5 6.236	6.789 0.147 11.61 1.71 1.690 7.0 2 6.231	6.785 0.147 11.603 1.71 1.697 7.5 28 6.194 6	6.739 0.148 11.591 1.72 1.709 0 28.5 152 6.1	6.692 0.149 11.578 1.73 1.722 29.0 49 6.11	6.603 0.151 11.556 1.75 1.744 29.5 3 6.110	6.556 0.153 11.538 1.76 1.762 30.0 6.074	6.508 0.154 11.519 1.77 1.781	6.503 0.154 11.511 1.77 1.789	6.462 0.155 11.502 1.78 1.798	6.460 0.155 11.498 1.78 1.802	0.156 11.491 1.79 1.809	22.5 6.415 0.156 11.482 1.79 1.818	23.0 6.373 0.157 11.477 1.829	23.5 3 6.368 0.157 1 11.462 8 1.8 9 1.838	24.0 6.366 0.157 11.458 1.8 1.842	24.5 6.364 0.157 11.455 1.845	0.1 11
6.838 0.146 11.625 1.7 1.675 6.319 .158	6.838 0.146 11.624 1.7 1.676 26.0 2.6.0 2.78	6.791 0.147 11.613 1.71 1.687 26.5 6.236	6.789 0.147 11.61 1.71 1.690 7.0 2 6.231	6.785 0.147 11.603 1.71 1.697 7.5 28 6.194 6 161 0.14	6.739 0.148 11.591 1.72 1.709 0 28.5 1.152 6.1 53 0.163	6.692 0.149 11.578 1.73 1.722 29.0 49 6.11	6.603 0.151 11.556 1.75 1.744 29.5 3 6.110 0.164	6.556 0.153 11.538 1.76 1.762 30.0 6.074 0.165	6.508 0.154 11.519 1.77 1.781	6.503 0.154 11.511 1.77 1.789	6.462 0.155 11.502 1.78 1.798	6.460 0.155 11.498 1.78 1.802	0.156 11.491 1.79 1.809	0.156 11.482 1.79 1.818	23.0 6.373 0.157 11.477 1.4 1.829	23.5 3 6.368 0.157 1 11.462 8 1.8 9 1.838	24.0 6.366 0.157 11.458 1.8 1.842	0.157 6.364 0.157 11.455 1.845	0.1 11
6.838 1.146 11.625 1.7 1.675 5.5 6.319 1.58 1.437	6.838 0.146 11.624 1.7 1.676 26.0 6.278 0.159 0	6.791 0.147 11.613 1.71 1.687 26.5 2.236 2.236 2.160 0 11.411	6.789 0.147 11.61 1.71 1.690 7.0 2 6.231 .160 0.1 11.403 1	6.785 0.147 11.603 1.71 1.697 7.5 28 6.194 6 161 0.11 1.397 11	6.739 0.148 11.591 1.72 1.709 0 28.5 152 6.1 53 0.165 382 11.3	6.692 0.149 11.578 1.73 1.722 29.0 49 6.11	6.603 0.151 11.556 1.75 1.744 29.5 3 6.110 0.164 7 11.364	6.556 0.153 11.538 1.76 1.762 30.0 6.074 0.165 11.358	6.508 0.154 11.519 1.77 1.781	6.503 0.154 11.511 1.77 1.789	6.462 0.155 11.502 1.78 1.798	6.460 0.155 11.498 1.78 1.802	0.156 11.491 1.79 1.809	0.156 11.482 1.79 1.818	0.157 11.47 1.829	23.5 3 6.368 0.157 1 11.462 8 1.8 9 1.838	24.0 6.366 0.157 11.458 1.8 1.842	0.157 6.364 0.157 11.455 1.8 1.845	0.1 11
6.838 1.146 11.625 1.7 1.675 5.5 6.319 158 11.437 1.81 1.437	6.838 0.146 11.624 1.7 1.676 26.0 6.278 0.159 0.159 0.159 0.159 0.159	6.791 0.147 11.613 1.71 1.687 26.5 2.6236 0.160 0 11.411 1.83	6.789 0.147 11.61 1.71 1.690 7.0 2 6.231 .160 0.1 11.403 1 1.83	6.785 0.147 11.603 1.71 1.697 7.5 28 6.194 6 161 0.14 1.397 11 1.84	6.739 0.148 11.591 1.72 1.709 0 28.5 1.52 6.1 53 0.163 382 113 1.85 1	6.692 0.149 11.578 1.73 1.722 29.0 49 6.11 4 0.164 76 11.3 85 1.6	6.603 0.151 11.556 1.75 1.744 2.29.5 3 6.110 0.164 17 11.364 1.86	6.556 0.153 11.538 1.76 1.762 30.0 6.074 0.165 11.358 1.87 1.258	6.508 0.154 11.519 1.77 1.781	6.503 0.154 11.511 1.77 1.789	6.462 0.155 11.502 1.78 1.798	6.460 0.155 11.498 1.78 1.802	0.156 11.491 1.79 1.809	22.5 6.415 0.156 11.482 1.79 1.818	0.157 11.47 1.829	23.5 3 6.368 0.157 1 11.462 8 1.838 1.838	24.0 6.366 0.157 11.458 1.842	24.5 6.364 0.157 11.455 1.8 1.845	0.1 11

ND(-COOH	i) - 100ppr	m Nickel n	itrate		1.5 days															
details/t	time(mi	in)			0.5		1.0		1.5	2.0)	2.5		3.0	3.5		4.0	4	4.5	5.0
		resistand	ce			13.057		13.202	13.	209	13.354	ŕ	3.361	13.511	13.	359	1	3.209	13.204	13.203
nductivity	y for 100	ppm Nicl	cel nitrat	e ND(-CO	0 0.077		0.076		0.076	0.0	75	0.075		0.074	0.075		0.076	(0.076	0.076
V						12.404	1	.2.410	12.4	416	12.419	1	2.426 :	12.430	12.4	124	1	.2.416	12.412	12.411
1	100	Calada Ang		01.0		0.950		0.940	0.9	940	0.93		0.930	0.920	0.9	930		0.94	0.94	0.94
13.3-V TOF 1	LUUDDU IV	lickel nitra	te ND(-CO	UH)		0.896		0.890	0.0	584	0.881		J.874	0.870	0.0	576		0.884	0.888	0.889
5.5	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5	10.0	10.5	11.0	11.5	12.0) 12	2.5 13	8.0	13.5	14.0	14.5	15.
13.201	1 13.06	0 13.05	56 13.05	55 13.05	7 13.0	54 13.05	53 13.20	1 13.2	204 13.20	9 13.3	55 13.35	6 13.359	13.2	01 13	1.653 12	2.911	12.907	12.9	04 12.7	67 12.7
2500	0.077	0.077	0.077	0.077	0.077	0.077	2076	0.07	2500	0.07/	0.075	0.075	0.07/		70 00		0.077	0.077	0.070	0.07/
12 400	0.077	0.077	0.077	0.077	0.077	0.077	0.076	0.07	0.076	0.075	0.075	0.075	0.076	0.0	207 11	205	12.20	0.077	0.078	0.078
12.40	9 12.40	17 12.40	JS 12.4	02 12.40	14 12.41	JI 12	4 12.40)9 12.4)4 0	04 00	10 12	42 12.42 02 0.0	2 0.03	+ 12.4	09 1	0.05	0.06	12.59	L 12.5	56 12.5 56 0.	04 12.3 07 0
0.94	0.5	3 0.80	0.0 17 0.80	95 0.5 18 0.89	6 0.80	ia nar	0 0.20	1 0.8	.54 0.: 88 0.88	/ 0.8	20 0.5	0.876	0.0	94 01 0	330 0	905	0.50	0.01	2 0.01	6 09
15.5	16.0	16.5	17.0	17.5	18.0	18.5	19.0	19.5	20.0	20.5	21.0	21.5	22.0	22.5	23.0)	23.5	24.0	24.5	25.0
12.763	12.761	12.614	12.605	12.471	12.460	12.328	12.316	12.18	8 12.185	12.058	12.052	12.046	11.923	11.9	22 11.9	20	11.917	11.917	11.914	11.796
0.078	0.078	0.079	0.079	0.080	0.080	0.081	0.081	0.082	0.082	0.083	0.083	0.083	0.084	0.084	0.084		0.084	0.084	0.084	0.085
12.38	12.378	12.362	12.353	12.346	12.335	12.328	12.316	12.3	1 12.307	12.299	12.293	12.287	12.281	12	28 12.2	78	12.275	12.274	12.271	12.268
0.97	0.97	0.98	0.98	0.99	0.99	:	. 1	. 1.0	1 1.01	1.02	1.02	1.02	1.03	1.	03 1.	03	1.03	1.03	1.03	1.04
0.920	0.922	0.938	0.947	0.954	0.965	0.972	0.984	0.99	0.993	1.001	1.007	1.013	1.019	1.02	20 1.02	22	1.025	1.026	1.029	1.032
25.5	26.0	26.5	27.0	27.5	28.0	28.5	29.0	29.5	30.0											
11.793	11.795	11.669	11.671	11.668	11.666	11.664	11.550	11.549	11.548											
0.085	0.085	0.086	0.086	0.086	0.086	0.086	0.087	0.087	0.087											
12.265	12.267	12.252	12.255	12.251	12.249	12.247	12.243	12.242	12.241											
1.04	1.04	1.05	1.05	1.05	1.05	1.05	1.06	1.06	1.06											
1.035	1.033	1.048	1.045	1.049	1.051	1.053	1.057	1.058	1.059	【表	33]	Nick	el 1	00p	pm v	vit	h NI	D-C	DOH	[

D (-COOF	4) - 50ppr	n Nickel I	nitrate			1.5 days														
etails/t	ime(m	in)				0.5		1.0	1	5	2.0		2.5		3.0 3	3.5	4.0		4.5	5.0
		resista	nce				18.646		8.933	18.3	57	17.550		17.301	17.051	17.292		17.297	17.300	17.543
luctivit	y for 50	opm Nic	kel nit	rate NI	D(-COO	0.054		0.053	0	.054	0.057	7	0.058		0.059 0	.058	0.058		0.058	0.057
							12.679	1	2.685	12.6	66	12.636		12.630	12.618	12.623		12.627	12.629	12.63
							0.680		0.670	0.69	90	0.72		0.730	0.740	0.730		0.73	0.73	0.7
3-V for 5	50ppm Ni	ckel nitra	te ND(-	COOH)			0.621		0.615	0.63	34	0.664		0.670	0.682	0.677		0.673	0.671	0.669
.5	6.0	6.5	7	.0	7.5	8.0	8.5	9.0	9.5	10.0	10.5	11.0	11.5	12.0	12.5	13.0	13.5	14.0	14.5	15.0
17.550	17.55	1 17.	553	17.804	17.807	17.556	17.810	17.806	17.815	17.807	17.554	17.295	17.054	17.047	16.812	16.800	16.567	16.557	16.545	16.314
057	0.057	0.05	70	.056	0.056	0.057	0.056	0.056	0.056	0.056	0.057	0.058	0.059	0.059	0.059	0.060	0.060	0.060	0.060	0.061
12.636	5 12.63	12.	538	12.641	12.643	12.64	12.645	12.642	12.649	9 12.643	12.639	12.625	12.62	12.61	12.609	12.6	12.591	12.583	12.574	12.56
0.72	2 0.7	2 0	.72	0.71	0.71	0.72	0.71	0.71	0.7	L 0.71	0.72	0.73	0.74	0.74	0.75	0.75	0.76	0.76	0.76	0.7
0.664	0.66	3 0.6	62	0.659	0.657	0.660	0.655	0.658	0.651	0.657	0.661	0.675	0.680	0.685	0.691	0.700	0.709	0.717	0.726	0.738
5.5	16.0	16.5	17	.0 1	.7.5	18.0	18.5	19.0	19.5	20.0	20.5	21.0	21.5	22.0	22.5	23.0	23.5	24.0	24.5	25.0
6.308	16.087	16.07	2 15	.861 ·	15.854	15.846	15.643	15.641	15.645	15.848	15.854	15.853	15.849	15.645	15.447	15.446	15.251	15.252	15.248	15.059
061	0.062	0.062	0.0	53 0	.063	0.063	0.064	0.064	0.064	0.063	0.063	0.063	0.063	0.064	0.065	0.065	0.066	0.066	0.066	0.066
2.557	12.548	12.53	6 1	2.53 1	12.525	12.518	12.514	12.513	12.516	12.52	12.525	12.524	12.521	12.516	12.512	12.511	12.506	12.507	12.503	12.499
0.77	0.78	0.7	8	0.79	0.79	0.79	0.8	0.8	0.8	0.79	0.79	0.79	0.79	0.8	0.81	0.81	0.82	0.82	0.82	0.83
0.743	0.752	0.764	0.	770	0.775	0.782	0.786	0.787	0.784	0.780	0.775	0.776	0.779	0.784	0.788	0.789	0.794	0.793	0.797	0.801
5.5	26.0	26.5	27.0	27.5	28.0	28.5	29.0	29.5	30.0											
5.058	15.245	15.054	15.052	14.870	15.05	1 14.868	14.861	14.682	14.674											
066 (0.066	0.066	0.066	0.067	0.066	0.067	0.067	0.068	0.068											
2.498	12.501	12.495	12.493	12.491	1 12.49	2 12.489	9 12.483	12.48	12.473											
	1182	0.83	0.83	0.84	4 0.8	3 0.84	i 0.84	0.85	U.85											



(3) 硝酸锌導電數據與曲線

ND (-COOH	l) - 200ppn	n Zinc nitra	ate																
details/t	ime(mir	ר)			0.5		1.0	1	5	2.0		2.5		3.0	3.5	4.0	4	1.5	5.0
	r	esistance	3			5.903	ł	5.797	5.6	96	5.631		5.562	5.463	5.400		5.334	5.304	5.273
onductivit	y for 200	ppm Zind	nitrate l	ND(-COO	0.169		0.172	0.:	L76	0.178		0.180		0.183	0.185	0.187	C	0.189	0.190
V						11.393	11	363	11.3	6	11.319	1	1.291	11.254	11.232		11.201	11.191	11.178
I						1.930	1	.960	1.99	90	2.01		2.030	2.060	2.080		2.1	2.11	2.12
13.3-V for 2	00ppm Zir	nc nitrate N	ID(-COOH	D		1.907	1	.937	1.96	54	1.981		2.009	2.046	2.068		2.099	2.109	2.122
5.5	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5	10.0	10.5	11.0	11.5	12.0) 12.	5 13.0	13.5	14.0	14.5	15.0
5.212	5.154	5.124	5.069	9 5.016	6 4.96	1 4.934	4.881	4.804	4.729	4.634	4.587	4.496	4.4	23 4.3	156 4.334	4.243	4.164	4.090	4.027
0.192	0.194	0.195	0.197	0.199	0.202	0.203	0.205	0.208	0.211	0.216	0.218	0.222	0.226	0.23	0 0.231	0.236	0.240	0.244	0.248
11.153	11.132	11.119	11.10	1 11.08	6 11.06	3 11.053	11.031	11.001	10.972	10.937	10.916	10.881	10.8	36 10.8	804 10.791	10.736	10.701	10.676	10.631
2.14	2.16	2.17	7 2.19	9 2.2	1 2.2	3 2.24	2.26	2.29	2.32	2.36	2.38	2.42	2.	45 2	.48 2.49	2.53	2.57	2.61	2.64
2.147	2.168	2.181	2.199	2.214	2.237	2.247	2.269	2.299	2.328	2.363	2.384	2.419	2.46	64 2.4	96 2.509	2.564	2.599	2.624	2.669
15.5	16.0	16.5	17.0	17.5	18.0	18.5	19.0	19.5	20.0	20.5	21.0	21.5	22.0	22.5	23.0	23.5	24.0	24.5	25.0
3.988	3.930	3.856	3.803	3.747	3.693	3.642	3.610	3.558	3.522	3.505	3.476	3.458	3.42	3 3.3	3.365	3.336	3.290	3.244	3.229
0.251	0.254	0.259	0.263	0.267	0.271	0.275	0.277	0.281	0.284	0.285	0.288	0.289	0.292	0.295	0.297	0.300	0.304	0.308	0.310
10.609	10.571	10.526	10.497	10.453	10.413	10.381	10.36	10.319	10.283	10.271	10.253	10.236	10.20	1 10.1	82 10.161	10.142	10.101	9.991	9.978
2.66	2.69	2.73	2.76	2.79	2.82	2.85	2.87	2.9	2.92	2.93	2.95	2.96	2.9	8	3 3.02	3.04	3.07	3.08	3.09
2.691	2.729	2.774	2.803	2.847	2.887	2.919	2.940	2.981	3.017	3.029	3.047	3.064	3.09	9 3.11	.8 3.139	3.158	3.199	3.309	3.322
25.5	26.0	26.5	27.0	27.5	28.0	28.5	29.0	29.5	30.0										
3.195	3.153	3.124	3.071	3.045	3.031	3.017	2.965	2.940	2.915										
0.313	0.317	0.320	0.326	0.328	0.330	0.331	0.337	0.340	0.343										
9.936	9.901	9.872	9.828	9.804	9.79	9.776	9.724	9.701	9.679										
3.11	3.14	3.16	3.2	3.22	3.23	3.24	3.28	3.3	3.32										
3.364	3.399	3.428	3.472	3.496	3.510	3.524	3.576	3.599	3.621	I ŧ	÷ 36	17	inc	200	Joom	wit	h N	D-C	OOF
										1	C 50	A 2		200	Phh				001



(4) 文字概述

觀察【表 31】、【表 35】與【表 39】可知奈米鑽石應有吸附 趨勢,如【註 4】文獻中提及,該實驗可利用導電率波動曲線 來分辨各種離子種類,而在奈米鑽石沉澱物上的清澈溶液經過 導電率分析明顯發現平穩趨勢。由於酸洗後奈米鑽石上方仍含 有 COOH 基,且在之後討論中本組的機制裡也有釋放離子的 可能,且因 Ni(50ppm)導電率並不高,故能推測【表 35】(50ppm) 導電度稍有上升趨勢原因。

(六) ND(酸洗後之奈米鑽石 ND-COOH)吸附不同重金屬之比較與錯離子吸 附比較

- 1. 多種單一離子
 - (1) 研究數據

ionic/cc	🔹 origin 💽	2.00 🔹	4.00 🔽	8.00 🔽	16.00 🔽	32.00 💌
Cu	2403.66	1201.83	600.92	300.46	150.23	75.11
Со	3535.42	1767.71	883.86	441.93	220.96	110.48
Pb	1158.98	579.49	289.75	144.87	72.44	36.22
Fe	838.73	419.37	209.68	104.84	52.42	26.21
Ni	3097.11	1548.55	774.28	387.14	193.57	96.78
【表 40】	ICP-MS 測出	之原始溶	液濃度(ppi	n)		
註:						
1. 2,等	數值表示稀释	睪倍率,而	origin表配	置的原樣本	經 ICP-MS	檢驗並推算

得知(原數據請見3.原始數據)

2.	此數據未考	慮到奈米鑽	石所佔有體積(鑽石	密度:3.52), 7	「面數據會先換算。
----	-------	-------	-----------	-------------	-----------

Copper	origin	after	differences
Cu	1400.81	1228.48	172.33
Cu	700.40	586.41	114.00
Cu	350.20	132.05	218.15
Cu	175.10	64.27	110.84
Cu	87.55	23.70	63.85

Cobalt	origin	ofter	differences
Coball	ongin	and	uniciclicits
Со	2060.38	1098.74	961.64
Со	1030.19	699.71	330.48
Со	515.09	348.39	166.71
Со	257.55	152.39	105.16
Со	128.77	56.81	71.96

T 1		0	1' 00
Lead	origin	atter	differences
Pb	675.43	67.81	607.62
Pb	337.72	268.41	69.31
Pb	168.86	77.68	91.18
Pb	84.43	29.91	54.52
Pb	42.21	16.85	25.37

Iron	origin	after	differences
Fe	488.80	316.95	171.85
Fe	244.40	156.53	87.87
Fe	122.20	54.02	68.18
Fe	61.10	20.92	40.18
Fe	30.55	2.67	40.18

Nickel	origin	after	differences
Ni	1804.94	1548.57	256.36
Ni	902.47	818.39	84.08
Ni	451.23	90.26	360.97
Ni	225.62	118.52	107.10
Ni	112.81	31.99	80.82

ion/dilute	2.00	-	4.00	-	8.00	Ŧ	16.00	-	32.00	Ŧ
Cu	172.3	3	114.()()	218.	15	110.8	84	63	.85
Со	961.6	64	330.4	18	166.	71	105.	16	71	.96
Pb	607.6	52	69.3	31	91.	18	54.	52	25	.37
Fe	171.8	5	87.8	37	68.	18	40.	18	27	.88
Ni	256.3	6	84.0)8	360.	97	107.	10	80	.82
【表 46】各溶液	吸附濃度	差異	展之比	較自	直					

(2) 研究數據整理

A. 綜合整理

- 在此表中明顯探討出各曲線差異:分為兩種:
 - a. Co,Fe 有類似於依數性質(濃度增加吸附率 增加)之特性
- ppm Cu 3000 2500 $v = 0.0013x^3 - 0.2826x^2 + 16.221x - 72.778$ 2000 1500 1000 500 0 25 33 41 49 65 73 81 83 81 83 81 83 97 97 97 97 1121 1121 1121 1121 1153 1153 201 103 201 10ppm -500 【表 47】硝酸銅吸附濃度比較與趨勢線 Pb ppm 60000 Pb 50000 $y = 0.0084x^3 - 0.669x^2 + 15.976x - 30.678$ 40000 30000 20000 10000 б 17-10000 10ppm 【表 48】硝酸鉛吸附濃度比較與趨勢線 Со ppm 1200 1000 $= 6E-05x^3 - 0.001x^2 + 2.3004x + 43.131$ 800 600 400 200 0 17 25 33 49 49 49 73 81 81 105 89 97 97 89 97 1105 1113 1113 1113 11132 11132 11132 11132 11133 201 10ppm 【表49】硝酸鈷吸附濃度比較與趨勢線
- b. 先上升下降又上升的特質(Cu Pb Ni)



B. 個別離子分析曲線圖【吸附前後差/最終吸附濃度】
在以下表格為吸附曲線
低與高即為濃度小到大的排列方式。
此次圖表所顯示為【吸附前後濃度差/最終濃度】
從表中了解鈷有最大的吸附率。
其他吸附粒子的情形因時間有限尚無機會作多次研究,將於報告繳
交後將做更多實驗以確認實驗正確性



2. 單一離子(Cu,Co,and Fe)於 SEM 下微觀

(1) 硝酸銅 Cu(NO3)2





在上圖中,以黃色圓圈圈出區域可看到很多奈米鑽石沉積。

(2) 硝酸鈷 Co(NO3)2





在黃色圓圈處是硝酸鈷吸附後的小型沉澱 (3) 硝酸鐵 Fe(NO₃)₃





看似平面的立體沉澱事實上仍由奈米鑽石小顆粒聚集而成,如上圖圓圈所指出。

3. 單一離子元素分析

(1) 硝酸銅



從上面2張分析可得總體而言氧佔的比例相對較高

(2) 硝酸鈷





氧的比例佔極高且鈷的比例與碳的比例相當。(Mapping 疊圖可看討論)



(3) 硝酸鐵



皆可測得鐵元素且比例相當

4. 錯離子化合物吸附情形

在此三種錯離子化合物內以銅氨錯離子吸附效率最為顯著、 鎳離子吸附效率亦達高點, 鈷氨錯離子吸附效率也不差, 可知 其不影響奈米鑽石的吸附功能, 更凸顯出專一性的吸附方式。

complex -	origina -	after
Cu(NH3)x	1203.56	288.84
Co(NH3)6	106.58	92.17
Ni(NH3)6	256.15	154.97

在圖中三種皆有變較淺色的情況,故推測可能為或是本身物質 差異。



(七) 重複利用討論

本組透過硝酸沖洗並利用 ICP-MS 確認吸附有釋放情形。

release	-	conc'	•	
Pb		601.1	23	
Ni		2012.4	43	【表 60】釋放數(

(八) 討論

- 1. 對於 LM324 系統改變之原因與相關實驗
 - (1)對於【註3】文獻方式之相關實驗
 - A. 先前推測與實驗目的

於過去的實驗中【註3】,本組提出大烏雲理論,意指 溶液導電度(電阻)變化原因是從壓克力箱注入端以一堆似 雲離子團的方式推移至負極。在這個假設下仍有一個問題: 為何溶液電阻曲線(當時並不用倒數取導電度)會呈現不規 則的震盪趨勢(上上下下重複),如上面圖表中重金屬水溶 液導電度所示。雖然這些不規則曲線為一種判斷金屬離子 的方式,且亦發現濃度並不影響曲線的形狀。賽後,本組 仍對此現象進行討論,並了解原因。

B. 實驗方法

相同於【註3】中的實驗,利用一個大型(長20公分)的 壓克力箱裝滿水,但改變距離,直接於邊處放置白金片組, 並接上LM324 實驗裝置。靜置5分鐘使其波浪平穩再加入 有顏色的溶液,分別為碘酒(多、中、少)與飽和硝酸銅溶 液,觀察注射後與受電場下的影響。

C. 實驗結果







碘(濃度中)之電解現象相關實驗 b.







- 【圖 77】放入少碘酒(50min)
- 硝酸銅之電解現象實驗



d.



(2)文字敘述

如圖上圖所示,此些皆有一項特點,即是分割面清楚,足 以用來證明其並不以大烏雲理論運作,對於其運作方式則可 藉由不同時間圖解釋,從上圖的時間變化亦可得知界面逐漸 模糊、並有明顯聚集情形,從碘的實驗中最為顯著。而是後, 本組亦得到良好解釋,亦即該溶液被吸起與產生之相關電化 學反應實為影響電導度之主要原因。

(3)研究改良

因本實驗顯示並不需要相當大之容器,主要為其中電化學 反應之相關影響,故本組決定以溶液直接加入的方式並以其 所造成的電阻變化作分析與結果論述。

2. 對於奈米鑽石與捕蟲囊表面覆蓋情形之討論與見解

在【圖 34】、【圖 35】可發現奈米鑽石的強烈吸附性,並得以推 估其對其他物質的吸附探討。



【圖 34】 bladder traps' reflection in $5\mu g/ml$'s ND solution.





3. 奈米鑽石生物共生性探討

(1)文獻探討

在奈米鑽石的應用方面已有許多生物方面探討,如【表 61】 所示。而應用方面多以其生物共生性為主,在一篇論文亦對 其在生物體內的 3D 移動情形探討,確定其絕不會進入細胞核, 且目前已有實驗研究證明奈米鑽石並不會對微生物的生長造 成影響。可反駁【註 5】的毒性假說。



(2) 實驗證明

適當的奈米鑽石並不會造成任意傷害甚有增加其活躍性情形,但若突然施以太多鑽石當然尚會對環境造成影響。所幸與本組實驗中探討出少數奈米鑽石即有強力吸附功效之事,增加 奈米鑽石吸附方面之實用性。見【圖 35】

 對於結果(二)、結果(三)與結果(四)無法看出規則性甚有導電率上 升趨勢之解釋與探討。

如【討論一】提及,本實驗之變素及原因即由該溶液內梨子濃 度、種類所致,各能表現其專一性質,如所有表格之繪圖,若該 溶液內尚有離子,則曲線差異不大,若該溶液內有其餘離子存在, 則將會影響數據顯示。本導電率變化測量方法,已在實驗中證明 個溶液內的離子變化,亦即此為一簡單測量分析方式,若該水質 內有離子變化將影響本組裝製數據曲線,屆時即可再透過更精密 的儀器進行內容物分析。

5. 硝酸鐵特殊情形

當奈米鑽石加入硝酸鐵溶液時會出現如右列的分離情形,經查 詢得知其密度最小,故不是因密度影響。本 組懷疑其已達飽和,並且不在與下面溶液反 應(奈米鑽石溶液成黃色)。【圖 81】



【圖 82】從此圖可知以作用的奈米 鑽石呈現黃色即為氧化後吸附於奈 米鑽石上的顏色顯現。



6. 氧化金屬吸附

從上頁得知氧化鐵的吸附,本組可再從 SEM 元素分析得各硝酸金屬化合物表格並透過疊圖分析金屬原子與氧原子分布情形,如下圖所示。由此可確定氧化金屬存在。

在外觀上即有顯著改變者有

- (1) 硝酸鐵:在離心後奈米鑽石皆產生黃色沉澱,表其吸附有氧化物。【圖 83】且在樣本製作上也可見強烈顯色效應。
- (2) 硝酸銅、鈷:樣本製作後可看見外圍顏色【圖 84】-【圖 85】



疊圖分析

- (1)由下圖可得 Fe(NO₃)₂、Cu(NO₃)₂和 Co(NO₃)₂疊圖分析結果,其 中可明顯得知在乾燥樣本中氧與金屬確實有產生化合,且此 亦可以成為本組吸附機裡的一大證據(離子交換)。
- (2) 硝酸鈷樣本含氧的比例極高竟然大於奈米鑽石的碳比例,亦 即氧應完全吸附在奈米鑽石表面此亦可從自製疊圖得知。





8. 奈米鑽石吸附機理

四、結論與應用

(一) 奈米鑽石吸附性質整理

- 1. 重金屬離子吸附
 - (1)離子種類專一性

在研究結果中本組從最簡易之檢驗法~LM324 導電率測 試至 ICP-MS 準確濃度皆可歸納出上述之吸附與導電曲線對 各種離子的專一性。

A. 導電率曲線專一性

本次實驗所運用之導電度測量方法確立對各種溶液成 分之專一性,故在本次實驗所運用之簡易測試方法可為一 檢驗吸附性質之簡易設備。

B. 吸附曲線專一性

在本組所繪製的吸附曲線中,對每種離子的吸附特性皆 可繪製出不同曲線分布,並如一般的吸附曲線相似,但本 組也發現有些點有特別高的趨勢,此次繪製圖裡並無將那 些點納入,然而本組也會在之後的時間中重複實驗以確保 實驗的準確性質。

(2)重複利用性

在本次實驗中所測得之奈米鑽石釋放離子濃度約 800-2012 ppm 左右,意指奈米鑽石上所吸附之重金屬離子可被洗出。 故其重複利用性可以確定。

(3) 錯離子化合物之吸附

在多篇文獻中,本組皆發現許多吸附器並無吸附錯離子化 合物之功能,然而本組數據顯示奈米鑽石極具錯合物吸附特 性,更增添奈米鑽石於現實吸附上之應用。

- 2. 巨觀、微觀觀察
 - (1) 巨觀觀察

本組能找到此方向之原因為加入重金屬溶液後,懸浮液內 的奈米鑽石有沉澱現象。後經實驗也證明奈米鑽石溶液可使 金屬氧化並吸附氧化物,而此亦可應用在定性分析之檢驗。

(2)微觀觀察

在 SEM 下的奈米鑽石有不同的外觀與聚集情形,故已證明 其有吸附特性,且各種離子會有不同的聚集性質。

- 3. 吸附假說(可參閱【討論8】)
 - (1)氧化吸附假說

本組在實驗過程內可了解到氧的比例會因不同的離子種類 而改變本組在【討論 6.】裡特對此事發表見解與看法,並相 信其是間接吸附的重要元素。

(2)酸根置換假說

在【討論 7.】內可了解到外觀差異也可以做為吸附依據, 此時可先觀察到有氧處不一定有重金屬,但有重金屬處常看 見氧,由氧與重金屬的堆疊圖【圖 86】~【圖 90】可得知氧 與重金屬的相對位置與數目,更能確定此假說之可能性。

(3)正、負電靜電吸引

本組由奈米鑽石在一般狀態下介面電位為負的特性推測此假說。

而奈米鑽石粒徑與方向也會影響一物(在此表離子)沉澱形 狀與結構。

- 4. 生物性質應用
 - (1)生物共生性

在最初黃花狸藻實驗中,本組可清楚點出黃花狸藻並不會 受奈米鑽石影響而失去其生存功能,甚至有許多共生微藻活 動力反而更加旺盛,由此得知其有生物共生性質。

(2)對植物體的附著

在前面提及的照片中可清楚看出奈米鑽石在捕蟲囊上的吸 附特性(一層)。然而其對為藻類、微生物類並不會造成影響, 可想見,捕蟲囊或表皮細胞上應有特殊官能基讓其進行吸附 即聚集。

(二)應用1. 本組繪製工程應用概念圖(左而右之設計)

在一工廠內設為兩管線,一為廢水入口二為恢復入口。

第一部分:當廢水進入時,靜置並等到奈米鑽石沉澱,透過連通管原理水會不段 循環,共分為二次吸附,最後出來的水將為含有重金屬離子低濃度之廢水。 第二部分:加入酸性物質(可來自工業廢水等)使整體 PH 值降低而釋放重金屬離子 (可見討論 8.)。 2. 本組繪製工程應用概念圖(吸附塔設計)

本設計透過薄膜過濾並過濾出最清潔之水溶液,如同常見吸附管,可交換吸附管 來達到重複利用與吸附效果。

五、參考文獻

- 李嘉祐、鄭楚玄。2010年。應用吸水高分子螯合重金屬離子及奈米銀的 製備。2010年臺灣國際科學展覽會優勝作品專輯。
- 莊淳喬、莊迪喬。2006年。水生開花食蟲植物絲葉狸藻捕蟲囊構造及共質 體運輸。台灣2006年國際科展展覽會研究報告書。
- 夏志豪、黃厚宜。2014年。利用L.M.S即時顯示系統建立資料庫,在重金 屬汙染監測上之應用。2014年台灣國際科學展覽會研究報告書。
- 4. 張煥正研究員。居禮夫人的寶石:螢光奈米鑽石。研究報告。
- 黃品慈、陳昕。2010年。奈米粒子對細胞與生物之毒性及其分布。2010年 臺灣國際科學展覽會優勝作品專輯。
- Vadym N. Mochalin, Olga Shenderova, Dean Hoand, Yury Gogotsi. DECEMBER 2011. The properties and applications of nanodiamonds. Nano Technology Review Article. NNANO.2011.209. p.11~p.20.

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ISEF 2015 Science Project Report

Abstract

With the growing concern over environmental issues and the rapid development of nanomaterials, a more efficient adsorbent for heavy metal removal is crucial. In our research, we used Nanodiamond (ND) made by High Temperature High Pressure (HTHP) process, and ran through acidified procedure to enhance NDs' carboxylic acid groups (-COOH) ratio, making Acidified Nanodiamonds (ANDs). ANDs was used as an adsorbent of heavy metals. The mechanisms and characteristics in the adsorption reaction were examined. The materials were characterized by several techniques, including IR spectroscopy, Scanning Electron Microscopy (SEM), Zetasizer, ICP-MS, confocal microscopy etc. For the purpose of being an environmental friendly adsorbent, biocompatibility is a crucial factor. We found that ND was not harmful to the creatures in aquatic environment, a fact verifiable when we added ND(aq) to algae, Ultracularia gibba. In term of the heavy metal removal, our results show that the adsorption capacity is varied with different metal ions, and special adsorption reasons are illustrated. In addition, the effect of the ND's concentration, pH and time of adsorption were all studied in our research. Reusability is another important factor to become a novel green adsorbent. ANDs is found to be reusable after adding nitric acid to the NDs precipitates. All these are consistent with the key elements of the Twelve Principles of Green Chemistry, which concerned Prevention, Nanodiamond as a Novel Green Adsorbent for Heavy Metal Removal

Atom Economy, Designing Safer Chemicals, and Renewable Feedstock.

Nanodiamond as a Novel Green Adsorbent for Heavy Metal Removal

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Finally, I would like to thank for all my classmates, teachers, and, most importantly, my parents, for encouraging and supporting me. This is the first project I contact with universities and laboratories by myself for fulfilling my dream. Thanks for everyone whom helped me and of course my old partner, Jerry Huang for your consideration; best listener, Andy Wang, for always comforting me when I am under pressure. Good luck~ Thanks!
I. Introduction

A. Motivation

Heavy metal contamination leads to a serious impact on the human society and eco system. The environmental remediation technologies play an important role in the recent era. I (the author) have been developing several heavy metal detection and analysis systems (Continuous Research) in my previous research, and I wished to develop or utilize a new material as an adsorbent in order to recover the environment. (Fig.1)



During last years' vacation, I am fortunate to have the opportunity to work on a research project "Biological Tracing and investigation of Utricularia Gibba's Digestion System by Fluorescent Nanodiamonds (FNDs)", and found that Nanodiamonds (NDs) have strong adsorption ability on plants. After several literature reviews, I found the carbon allotropes may hold the key to enable a "GREEN" future including biocompatibility, and reusability, which reflects that NDs may be a good adsorbent for heavy metal removal!

B. Objectives

Engineering Aspects

- 1. Developing high-efficiency adsorbent for the removal of heavy metal ions
- 2. Manifesting the biocompatibility and reusability of the adsorbent

Scientific Aspects

1. Understanding the adsorption mechanism and make further experiments for manifesting

II. Scientific Problems and Questions

Engineering Problems

- 1. It is crucial to find an adsorbent which can achieve high atom economy (high removal of heavy metal ions).
- 2. Nano particles (NPs) as a heavy metal adsorbent was not prevalent before due to the cytotoxicity of other NPs.

Scientific Questions

- 1. Investigate whether the Acidified Nanodiamonds has carboxylate group and are able to adsorb heavy metal ions.
- 2. If so, what is the adsorption mechanism of Nanodiamonds?

III. Instrumental and Experimental

A. Experimental Instruments and Sample Preparation

Scanning Electron Microscope (SEM) and Electron-Dispersive X-ray Spectroscopy (EDX)

Field Emission Scanning Electron Microscope (NOVA NANO SEM 450, Fig.2b) is used in this research for surface morphology imaging. The basic principle for SEM is based on the reflection of the electron which is shot by the electron gun [powered by the magnetic field] (Fig.2a). The types of signal include Secondary Electron (SE) [Secondary means that the electron is not the primary electron (the electron emitted)], Backscattered Electron (BS)[the opposite motion of the incident electron], and X-Ray reflection (X-Ray) by different angle and orientation. The SEM image is due to the measurement of the SE's reflection angle. The EDX analysis is based on the energy radiation for filling the hole.(Fig.3) The sample were dried, put on the carbon paste, and covered with platinum



Fig.2 SEM (a) Explanations^[4] (b) NOVA NANO SEM 450



Fig.3

Simple Explanation for EDX spectroscopy

> Confocal Microscope

The basic principles of a Confocal Microscopy is to detect the light which is reflected from the sample. If we need to look in the fluorescent (for instance, in biocompatibility research, we utilize this technique for tracing), the light emitted can be controlled in several wavelength. In this research, confocal imaging was carried out using a SP5 inverted microscope (Leica) equipped with three solid-state lasers operating separately at 561nm for the excitation of FND. The bladder traps on the *Ultracularia Gibba* were made into water treated specimen.



> Inductively Coupled Plasma Mass Spectroscopy (ICP-MS)

The basic principles of ICP-MS is by using ICP to ionize, and utilize different engineering skills (Ex: Let ions collide with helium

to decrease impurities, or by using different charges to separate targeted ions) to filter the impurities (Fig.5). In this study, we prepared different standard solution (Pb²⁺, Cu²⁺, Ni²⁺, and Co²⁺) with 6 concentrations (0 ppb, 10 ppb, 20 ppb, 30 ppb, 40 ppb, and 50 ppb) for drawing the calibration curve, and dilute sample into range 0 ppb - 50 ppb for ICP-MS (Aligent 7700) measurement.



Fig.5 An Illustration of The ICP-MS^{[1][8]}

Fourier Transform Infrared Spectroscopy (FT-IR) and Ultraviolet Visible Spectroscopy (UV-Vis)

Both spectroscopy measure the transmittance amount after penetrating the sample. The data were gained in transmittance (%) or absorbance [(100-transmittance)%], and I was able to convert PRN file into excel and draw diagram by ourselves. Before Nanodiamond as a Novel Green Adsorbent for Heavy Metal Removal measurements, it is necessary to dry the sample (NDs) and add potassium bromide (ratio of sample and KBr=0.2%-1%) to enhance the transparency of the sample. The measured range of FT-IR falls on 700 cm⁻¹ to 4000 cm⁻¹. UV-Vis sample is placed in a small column and putted in the UV-Vis spectroscopy. In order to get accurate concentration (Optimized Conditions' Experiment: Co²⁺ analysis), standard solution (0, 200, 400, 600, 800, and 1000 ppm Cobalt Nitrate) are tested for calibration. The wavelength range which are proportional to the Co²⁺ concentration falls in 510nm-515nm.

Zeta Potential Analyzer

By looking at the dynamic scattering pattern (Fig.6), the Zeta Potential Analyzer is able to measure the size distribution of the particle. In the optimized condition – pH influences experiment, this instrument (Zetasizer-3000HS, Malvern) is used for identifying the zeta potential changes among different value.



Fig.6

An Illustration of the Influences by the Particle Size Distribution^[10]

B. Preparation of Nanodiamonds and Surface Modification

> Introduction to NDs production

Plasma Enhanced Chemical Vapour Decomposition (PECVD), detonation, High Pressure High Temperature (HTHP) process...etc. are usual routes for NDs production. The main idea for these methods are by making the precursors (Ex: PECVD, detonation process add methane. HPHT process uses the carbide on the surrounding.) discrete into single elements and go through the nucleation process to make precipitates (Fig.7A)

In this study, NDs (Micron+MDA, Element Six) were produced by HPHT process by adding high pressure (30 GPa) on two carbide anvil and making temperature differences (5-30 celcius) on both carbide anvil (upper carbide: 1500 K) (Fig.7B).



Fig.7 HPHT process(A) A simulation of the NDs production(B) HPHT instruments ^[3]

> Introduction to FNDs production

1. Turn NDs into FNDs : [Ion irradiation]

Use Ion beam to add helium into the NDs structure, and make carbon into nitrogen. After making a C-N-C structure, annealing is used to remove carbon and make N-V (V for vacancy), producing Ion-irradiated FNDs. In the biocompatibility experiment, FNDs were produced by radiation damage of type Ib diamond powders Nanodiamond as a Novel Green Adsorbent for Heavy Metal Removal (Micron + MDA M0.10, Element Six) using a 40 keV He²⁺ ion beam, followed by thermal annealing at 800 Celcius, air oxidation at 450 C and purification in concentrated H2SO4–HNO3 (3:1, vol/vol) solution at 100 Celcius.

2. Produce NDs:

Add Nitrogen in the production (PECVD, HTHP) of NDs, in order to make the nitrogen in diamond structure naturally.

> Preparation of Acidified Nanodiamonds (ANDs)

- 1. Acidified Process (Fig.8)
 - 1) Nanodiamonds were synthesized by high pressure high temperature process [30 GPa, 1500 K].
 - 2) Acidified Nanodiamonds were prepared by treating the nanodiamond with nitric acid (2M) and sulfuric acid (2M) for three hours.



Fig.8 An illustration of the ANDs producing process

- 2. Expected Results: ND-COOH functional groups
- 3. The results were characterized by SEM and IR spectroscopy.

C. Adsorption Process and Mechanisms

The adsorption experiments focused on four divalent metal ions $(Pb^{2+}, Cu^{2+}, Ni^{2+}, and Co^{2+})$, the environmental conditions were under 300K 0.5 mg/ml ANDs solution. The morphology and surface characterization were under research by SEM and FT-IR respectively.

D. Green Chemistry Concepts

> Biocompatibility:

Utricularia gibba, a shallow water vegetation, were used to test the biocompatibility of ANDs by adding FNDs in algae, and the bladder traps of the algae have been taken for investigation under confocal microscope.

> Reusability:

The used NDs (AND- M^{n+} , M^{n+} for metal ions) were treated with nitric acid. The functional groups of washed ANDs were investigated by FT-IR, and the adsorption efficiency was measured by UV-Vis.

IV. Results and Discussion

A. ANDs Characterization

Two criteria were used to analyze the characterization of ANDs.

1. SEM:

The size of ANDs aggregate was found between 80-100 nm (Fig.9).



Fig. 9 SEM Image of Nanodiamond Aggregation

2. FT-IR Spectra: (Fig.10)

- (1) Our expected results (ND-COOH) are identified.
- (2) ANDs also possess nitro groups.



Fig.10 FT-IR spectrum of ANDs

B. Adsorption Experiments (Fig.11)

- (1) ANDs have high efficiency towards Co^{2+} .
- (2) Adsorption amount increases with the initial concentration.



Fig.11 Adsorption Curves of Co²⁺, Cu²⁺, Ni²⁺, Pb²⁺

C. Adsorption Mechanism

1. SEM image of AND-M²⁺

- (1) After adsorption, SEM shows that ANDs' single particle (Fig.12A-C) are smaller than the original ones (Fig.12D).
- (2) The ANDs Co^{2+} is highly aggregated compared to other ANDs M^{n+} .



Fig.12 SEM images of ANDs-Mⁿ⁺ (A) Co²⁺ (B) Cu²⁺ (C) Pb²⁺ (D) Control

(3) We posed one hypothesis

- A. ANDs will re-disperse after adsorption, enhancing the adsorption capacity [result in IV. B]
- B. The higher adsorption capacity ANDs M^{n+} domains, the more aggregated nanodiamond morphology it reflects.

We can assume if we add higher $[M^{n+}]$ in solution, which results in extremely high adsorption capacity, the nanodiamond is going to be more aggregated. (IV. C. 4.)

2. EDX spectra of AND-M²⁺

EDX spectra (insets to Fig. 12) confirm the adsorption of Co^{2+} , Cu^{2+} , and Pb^{2+} .

- 3. FT-IR spectroscopy of AND-M²⁺
 - Disappearance of the CO peaks and broadening of OH peaks reveal the coordination of Mⁿ⁺ with carboxylate group. (red region in Fig.6)
 - (2) Due to the Co²⁺ NO₃⁻ interaction, no repulsion occurs between ANDs (yellow region in Fig.6) and



Fig.13 FT-IR spectra of ANDs-Mⁿ⁺

4. AND-Co²⁺ Morphology by SEM (Fig.14)

Three concentration (500ppm, 5000ppm, 50000ppm) of Co^{2+} are added into ANDs solution to test if the hypothesis we posed **(IV. C. 1. (3))** is right.

- The higher [Co²⁺] is concentrated, the smaller ANDs particle is observed.
- (2) The higher $[Co^{2+}]$ is concentrated, the more aggregation phenomenon is observed.

We proved that our assumption is right!



Fig.14 SEM images of ANDs-Co2+

Cobalt Nitrate Concentration: (A)(B) 500ppm (C)(D) 5000 ppm (E)(F) 50000 ppm

D. Optimized Condition for Adsorption

1. Equilibrium Time

Removal efficiency of Co^{2+} reaches maximum values after 20 min. (Fig.15)



Fig.15 Kinetics of Co²⁺ Adsorption

2. pH influences

Adsorption capacity enhanced with increasing pH value from pH 2.50-4.00. (Fig. 16)

At pH value greater than 3.00, negative charge on the surface of ANDs were observed, thus the interaction with Co^{2+} increased.



Fig.16 Zeta Potential and Co2+ Adsorbed Amount With Their Correspondence

3. Adsorbent Quantity

The maximum adsorption occurs at 0.25 mg/ml of ANDs solution.

The Co^{2+} adsorption capacity increases with amount of ANDs from 0.06 to 0.25 mg/ml. Further increase of the ANDs dosage did not substantially increase the adsorption of Co^{2+} .



Fig.16 Effect of ANDs Amount on Co²⁺ Adsorption as a Function of ANDs Initial Concentrations.

4. Temperature Effects

Though the adsorption process is endothermic, the temperature effect is not significant. (Fig.17)



Fig.17 Temperature Effect on Co²⁺ Adsorption

E. Green Chemistry Concepts

1. Biocompatibility

Though the FNDs were adsorbed in the stem of *Utricularia gibbas* (Fig.18A,B), the activity of microorganisms was not affected by FNDs(Fig.18C).



Fig.18 Confocal Microscope Images of FNDs Treated Bladder Traps
(A) Utricularia gibbas' stem (B) Utricularia gibbas' bladder trap
(C) Viable microorganisms in Utricularia gibbas' bladder trap

2. Reusability

- (1) The observation of CO functional group indicated that ANDs were regenerated after treating with nitric acid (Fig.19).
- (2) The adsorption capacity was retained after regeneration (Fig.20).





Reflects the Surface After Regeneration

Fig.14 Reusability Chart

V. Conclusions

- 1. Surface carboxylate functional group is the key factor for heavy metal removal.
- 2. ANDs are effective adsorbents for Co²⁺ removal, probably due to the interaction of NO₃⁻ ions.
- **3.** A special re-dispersion and aggregation phenomenon were observed in this research.
- The optimized condition for Co²⁺ adsorption was found to be pH>2.5, 20 minutes adsorption time, and at 0.25 mg/ml of ANDs.
- 5. ANDs are biocompatible and reusable, meeting the criteria of Green Chemistry

VI. References

- Agilent Technologies Announces Launch of the World's First Triple Quadrupole ICP-MS. Retrieved: May Seventh 2015 From:<u>http://www.measurementest.com/2012/01/agilent-technologies-announces-launch.html</u>
- A. M. Schrand, H. Huang, C. Carlson, J. J. Schlager, E. Ohsawa, S. M. Hussain, and L. Dai. Journal of Physical Chemistry B 111 (2007) 2-7
- Diamond Synthesis by HPHT Process. Retrieved: May Seventh 2015
 From :<u>http://www.substech.com/dokuwiki/doku.php?id=synthetic_diamonds</u>
- How a Scanning Electron Microscope Works? Retrieved: May Seventh 2015 From: https://www.youtube.com/watch?v=VWxYsZPtTsI
- M. Hadavifara, N. Bahramifar, H. Younesi, Q. Li. Chemical Engineering Journal 237 (2014) 217–228.
- O. Shenderova, A. Koscheev, N. Zaripov, I. Petrov, Y. Skryabin, P. Detkov, S. Turner, and G. Van Tendeloo. Journal of Alloys and Compounds 115 (2011) 9827–9837.
- T.A. Dolenko, S.A. Burikov, K.A. Laptinskiy, T.V. Laptinskaya, J.M. Rosenholm, A.A. Shiryaev ,A.R. Sabirov, I.I. Vlasovf. Journal of Alloys and Compounds 586 (2014) 436–439.
- The Principles of ICP-MS Retrieved: May Seventh 2015 From: https://www.youtube.com/watch?v=MQqtV2oiC6U
- V. N. Mochalin, O. Shenderova, D. Hoand, Y. Gogotsi. Nature Nanotechnology 209 (2011) 11-20.
- Wikipedia: Dynamic light scattering. Retrieved: May Seventh 2015 From:<u>http://en.wikipedia.org/wiki/Dynamic_light_scattering</u>

Y.R. Chang, H.Y. Lee, K.C, C.C Chang, D.S. Tsai, C.C F, T.S. Lim, Y.K Tzeng,
 C.Y. Fang, C.C. Han, H.C. Chang, W. Fann. Nature Nanotechnology 3 (2008) 284

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本實驗以奈米鑽石進行水中重金屬離子吸附實驗,由於奈米鑽 石之表面功能甚多,有助於加強水中重金屬離子之吸附,本研究實 驗完整且考慮其重複再利用可行性,是一個具有創意完整的研究。